NAVAL AVIATION SYSTEMS
TEAM

Naval Aviation Materials Team

Papers presented at special session "Naval Air Systems Team Advanced Materials Requirements, Programs, and Initiatives"

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Encl: (1) Session and Related Papers

     The enclosed technical papers were presented during the
subject conference one day session. The topics are the result of
the Naval Air Systems TEAM Materials Management Board's
efforts to highlight the critical issues in naval aviation
materials. Subject papers utilized the expertise across the entire
TEAM to provide a TEAM-wide perspective to industry,
academia and government activities. These papers summarize
the state-of-the-art in key areas of naval aviation materials
technology. If you would like additional information please do
not hesitate to call Mr. Jim Bethke at 301-342-8070.

                              Respectfully,

                              Dale L. Moore
                              Director, Materials Division
                              TEAM-4.3.4

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NAVAL AIR SYSTEMS TEAM
ADVANCED MATERIALS REQUIREMENTS, PROGRAMS AND INITIATIVES

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ABSTRACT

Naval aviation is facing some of it's most complex and difficult challenges in recent history. The Navy's harsh, corrosive environment combined with the demands of carrier and sea-based operations have always been formidable factors. Today, the continuing evolution of performance-based requirements in addition to emerging environmental and safety requirements are adding significantly to the Navy's challenge. Affordability is now an overarching consideration across the broad spectrum of naval aviation science and technology, acquisition development, production and in-service engineering activities. These synergistic requirements are driving the programs and initiatives of the Naval Aviation Materials Competency. This paper describes the complex scenario facing the naval aviation community, and the Materials Competency plans, programs and initiatives to meet the requirements of today as well as those anticipated for tomorrow.

KEY WORDS: Naval Aviation, Materials, Processes, Metals, Materials Protection, Composites, Corrosion, Nondestructive Test and Evaluation, Environmental

1. INTRODUCTION

The Naval Aviation Materials Competency is facing a difficult and complex set of technical and managerial challenges:

1) The Navy's uniquely harsh, corrosive environment coupled with the demanding challenges of carrier and sea-based operations pose one of the most adverse operational scenarios known in aviation.

2) Newly emerging technical requirements such as multi-service/multi-mission platforms, all-weather capable systems, environmental and safety regulations, condition-based maintenance, increased electromagnetic operating environments and requirements for signature control.

3) Reduced procurement budgets which extend aircraft use beyond their originally anticipated lifetimes.

4) Reduced science, technology and acquisition development budgets coupled with increased performance requirements as well as reduced maintenance.

The breadth of science and technology requirements to be addressed given these conditions is considerable. In today's era of downsizing these exists an increased sensitivity to acquisition cost; schedule and performance risk; reduced development, procurement and maintenance funding; aging aircraft; and more complex threats. The Naval Air Systems TEAM Materials Competency has developed a series of strategies to help meet these challenges through the development and transition of critical, enabling technologies focused on the specific needs of naval aviation. These strategies are driven by the underlying need to maintain safety-of-flight integrity and mission effectiveness, all at an affordable cost. The strategies include:

1) Effectively integrate and focus science and technology, acquisition engineering and in-service support programs and resources.

2) Streamline advanced technology transition and certification.

3) Form collaborative partnerships with the joint services, government activities and industry to better leverage and focus available resources.

4) Address affordability as an integral component in all of our activities.

Advanced materials and processes are a fundamental component in the Naval Air Systems TEAM's ability to meet its requirements across a broad array of applications including air vehicles, propulsion, and electronics. Advanced materials have a direct impact on operational performance and affordability throughout the entire life cycle of systems development, production and in-service support. To fully appreciate the profound effect that materials and processes have on naval aviation systems, it is necessary to understand the Navy's unique environment and its impact on systems and operations. It is also important to understand the more contemporary, external influences which impact our ability to meet the Navy's mission including the overarching requirement for life cycle affordability.

2. REQUIREMENTS

2.1 Naval Aviation Environment Navy ship-based aircraft must do everything that land-based aircraft do, but in a more hostile environment under more adverse conditions. Catapult take-off and arrested landings require quick and precise engine control. Engines are highly susceptible to steam and foreign object ingestion. Aircraft are weight limited and are exposed to severe high impact loading. Carriers have very limited space for stowage and maintenance which limits the types of aircraft deployed and drives flexibility and adaptability, as well as commonality of spares and support equipment for maintenance. Maintenance is performed at the lowest level possible to minimize aircraft movement on the carrier.

The synergistic effects of salt air, stack gases, white water, elevated and cryogenic temperatures, elevated humidity, steam, sand, and dust create the most hostile and challenging environments for aviation operational systems in the world. The structural and nonstructural materials selected for naval aviation systems are required to meet stringent operational performance and durability requirements with minimal maintenance.

The Navy's maritime environment directly impacts every material and process selection for our advanced systems. Materials compatibility, galvanic isolation, sealing, and resistance to temperature, humidity, operational chemicals are strong considerations in the material selection

process. Materials protection technologies are vital to sustaining an affordable operational force. The operational fatigue life of metallic components can be affected by this corrosive environment. Stress corrosion and hydrogen embrittlement can prematurely initiate and accelerate the propagation of cracks. Advanced composites used at temperatures between 300°F and 450°F typically require the use of imide-based polymers. However, these resins have been shown to dramatically degrade in a corrosive environment when applied in a strong galvanic couple such as graphite and aluminum. Sealants and adhesives play a crucial role across a number of fronts. They control the intrusion of harmful corrodents as well as provide corrosion protection between potentially dissimilar materials. At the same time, sealants and adhesives must maintain critical electromagnetic shielding for safe operation of flight controls and electrical systems. Newly emerging requirements such as all-weather, day or night operations combined with signature control and higher power electrical systems stress the need to meet and maintain stringent control of electrical characteristics in an otherwise degradative environment. Additionally, shipboard operations provide many opportunities for aircraft handling damage. Damage must be rapidly inspected and repaired either on the flight deck or in severely confined spaces. Naval aviation propulsion materials must cope with severe hot corrosive conditions from steam injestion combined with a variety of sea-based salts. Also, aggressive erodents such as sand and dust are frequently encoutered due to routine low level flight operations.

2.2 Environmental and Safety Requirements Naval aviation must comply with federal, state and local environmental and safety regulations including Executive Order 12856 which drives the use and procurement of the least hazardous materials. These requirements have a profound impact on the production, operation and maintenance of Naval aviation systems. Environmental regulations which drive down the amount of Volatile Organic Compounds and Hazardous Materials used impacts naval aviation in a number of ways. Of particular importance is the ability to eliminate or minimize the degradation of our fielded systems in the Navy's harsh corrosive environment. Corrosion resistant adhesives, sealants, organic and inorganic coatings and protective systems often rely on chromium for passivation. Examples include corrosion resistant sealants, adhesive primers and conversion coatings. Chromium, our principle means of corrosion protection for airframe and propulsion systems is characterized as a toxic, heavy metal and is therefore recommended as a high priority for elimination. Concurrently, protective coating systems have relied on volatile organic compounds as a solids carrier to ensure controllable coating application. These V.O.C.'s must be dramatically reduced and eventually eliminated to meet environmental compliance regulations.

Prior to their elimination or replacement with safer alternatives, hazardous effluent and waste materials which are used in the production and maintenance of Naval aviation systems must be properly handled and can be very costly. For example, methelyne chloride, a suspected carcinogen, has been a mainstay in aerospace maintnance as a highly effective paint stripper. Methelyne dianaline, also a suspected carcinogen, is used as a curing agent for elevated temperature capable polymers including resins used in advanced composites.

As the cost to dispose and treat these materials continues to rise, the need for environmentally friendly materials and processes which perform equal to and better than the current state-of-the-art are essential to meeting performance and affordability requirements. The ability of Naval aviation to affordably meet our mission requirements today and in the future depends on our ability to develop, certify and transition environmentally compliant and safe high performance materials and processes.

2.3 Affordability The decline of Department of Defense resources impacts virtually every aspect of Naval aviation. Aggressive approaches to minimize acquisition and maintenance costs

have and will be implemented to continue to meet critical mission requirements. Reductions in the infrastructure to support and maintain our systems coupled with the reductions in development and acquisition budgets are driving significant changes in the way the Naval Air System's TEAM conducts its business. Every component of our business is evaluated for possible cost reduction or avoidance, but never at the expense of flight safety. These changes include base consolidation, acquisition streamlining and reform, implementing a Competency Aligned Organization (CAO) as well as increasing reliance on Joint Service and industry collaborative programs.

The risks associated with resource reductions should be examined at each phase of the acquisition life cycle to help improve the allocation of available resources. The impact of reduced science and technology resources lies at the foundation of our advanced systems development and support. Without a firm science and technology foundation to meet aggressive program affordability and performance goals, programs can proceed at increased cost, schedule and performance risk. As acquisition program costs become increasingly limited, programs may be limited to support only core activities vs. the proactive efforts to meet affordability and technical risk reduction goals. As acquisition programs are driven to shorter schedules, adequate risk reduction becomes increasingly difficult. As budgets reduce systems procurement and maintenance resources, there will be increased emphasis on supporting an aging fleet inventory more affordably.

From a materials and processes perspective, there exist significant opportunities to help meet these challenges. Initiatives ranging the entire spectrum of materials and processes including the conversion to commercial and performance-based procurement specifications to TEAM-wide integration via the CAO maximizes the effectiveness of our personnel, our capabilities and the programs and initiatives we undertake to meet our goals. Strong acquisition program involvement via the transition to business-like arrangements and personnel empowerment provide our acquisition programs with the technical expertise they need as an integral part of each program team. This Integrated Product Team approach significantly streamlines program execution while improving opportunities for science and technology transition and implementation. Acquisition streamlining allows Program Managers for Aircraft (PMA's) the flexibility to tailor program plans and strategies to meet stated goals and objectives. Affordability is now the forcing function which drives the evaluation, development and acceptance of new technologies and paradigms in naval aviation. Affordability is now a key requirement which will impact every aspect of naval aviation in the foreseeable future and is now a predominant theme for science and technology, acquisition development and production, and in-service support and engineering activities.

2.4 Acquisition Development/System Performance Requirements Despite the Navy's harsh maritime environment and the demands of carrier and sea-based operations, naval aviation aircraft and weapon systems must meet the same level of operational performance, readiness and mission effectiveness inherent in today's advanced weapon systems. Air vehicle thrust-to-weight, range, payload, maneuverability, survivability and lethality drive air vehicle performance and carrier suitability. Required thrust-to-weight ratios are being met through highly integrated air vehicle design processes using state-of-the-art materials, processes, structures, aerodynamics, survivability, vulnerability, subsystems, propulsion and electronics. As acquisition development costs and schedules become increasingly constrained, more effective means of defining requirements, optimizing and streamlining development processes, and transitioning enabling technologies into production becomes more critical.

Materials and processes are an integral part of the acquisition development cycle. Several critical considerations should be further explored.

The Concept Exploration and Definition Phase must provide a requirements and risk basis for the selection and development of the advanced materials and processes for the system. It is important at this stage to begin to solidify critical requirements which will drive material and process selections. Projections should be made regarding the transition of material candidates into anticipated applications including structural design and manufacturing.

The Demonstration and Validation Phase must now fully define material and process selections for specific applications. The development of critical, risk reduction data will eliminate potential showstoppers so that the program can proceed at minimum risk into Engineering and Manufacturing Development (EMD). Essential materials properties and processing characteristics must be evaluated to improve the fidelity of EMD weight and manufacturing cost estimates.

The EMD Phase of the program will be expected to adhere to a very aggressive Program Master Plan with a variety of metrics which are closely monitored to assess program health and progress. Significant variations in cost, schedule or performance can increase program risk. Materials and processes are at the foundation of this activity. A rigorous materials selection and development program which addresses critical risks upfront is essential to program success. Materials and processes certification requires the definition and acceptance of critical data which in broad terms consists of: materials and processes requirements definition, application criteria, materials properties and structural design allowables, materials and process specifications, manufacturing demonstration and first article destruct tests, nondestructive inspection for all structurally significant defects, and structural building block tests of representative verification articles including in most cases full scale static and fatigue testing.

The transition to Production from EMD includes certification of production representative materials, processes and structural design features which change as a result of EMD. Of particular importance for production certification are the tools required for production which must address durability, processibility and cost for the program.

The Naval Air Systems TEAM, in conjunction with the Air Force have developed a Joint Materials and Processes Specification. This specification is unique in that it is performance-based and incorporates both Navy and Air Force requirements. Equally important are the compilation of lessons learned on materials and processes selections, design development and application, and safety-of-flight certification. The Naval Air Systems TEAM uses an evolutionary building block methodology which is tailored for each application to maximize program resources while building sufficient technical confidence at minimum cost, schedule and performance risk.

As acquisition programs become increasingly sensitive to cost, schedule and performance risks as well as more cost and schedule constrained, new approaches to materials and processes will be necessary. Materials and process selection and development will require greater integration with design, manufacturing, survivability and logistics. New materials and processes which offer significant advantages in performance, durability and affordability will be uniquely suited to address these needs. High fidelity materials and process modeling and simulation are expected to be an essential component to reduce program development and production risks and costs. Innovative materials testing and design methodologies which address many of the shortfalls of our current way of doing business will be required to more accurately predict a material's behavior in a design application as it performs in the Navy's environment. Improved manufacturing processes and quality control will be required to reduce the costs associated with process variation and nonconformance. Cost effective, high fidelity nondestructive evaluation

technologies will be required to ensure safety of flight for innovative structural and manufacturing concepts. Unitized structure offers the potential for reduced assembly and overhead costs while optimizing structural design and associated weight. Materials and processes offer enabling capabilities to address the complex requirements we face today and in the future.

3.0 MATERIALS AND PROCESS PROGRAMS AND INITIATIVES

3.1 Materials and Processes To meet Naval aviation's complex set of requirements, the Naval Aviation Materials Competency is developing and transitioning a broad spectrum of technologies with direct impact on our current and future acquisition programs and fielded systems. Materials Competency technical activities are highly coordinated via a number of channels including the Navy Council on Materials and Structures, Acquisition Environmental Product Support Team, Lead Maintenance Technology Centers, Naval Aviation Science and Technology Office - Product Line Teams, Navy Manufacturing Technology Centers of Excellence as well as Joint Service activities.

Technology transition targets for advanced materials and processes can be divided into three sets of platforms: existing, development, and future. Numerous opportunities are available for existing platform technology transition including: F-18 C/D, F-14, AV-8B, P-3, S-3, E-2, EA-6B, H-53 and SH-60. Current EMD development platforms include: F/A-18 E/F, V-22, P-3 SRP, H-1/UH-1 4BN/BW Program, Joint Stand-off Weapon (JSOW), Joint Direct Attack Munition (JDAM), Joint Advanced Strike Missile (JASM), and the Standoff Land Attack Missile - Extended Range (SLAM-ER). Programs in the early stages of acquisition development are the Joint Strike Fighter (JSF) which includes Navy, Marine Corp. and Air Force variants, the Common Support Aircraft, and the Joint Replacement Aircraft. The thrusts of the Materials Competency are structured to address the entire life cycle of these principle programs. These activities are focused in three principle areas: Air Vehicle, Propulsion, and Electronics.

3.1.1 *Air Vehicle* Within the air vehicle component of Materials Competency Programs, a number of enabling initiatives are underway. In advanced composites, the Composite Affordability Initiative is a Joint Air Force/Navy effort to develop the tools and technologies necessary for the next generation of advanced composites. Currently, the CAI is directed toward impacting the Joint Strike Fighter (JSF) Engineering and Manufacturing Development program. The CAI is divided into three efforts: the JSF Technology Transition, the Fast Track Demonstration, and the Pervasive Technologies which are precompetitive efforts for the entire industry. CAI is a national industrial base initiative which leverages industry and government resources to collectively develop the tools and technologies necessary to take full advantage of the attributes of composites. Naval aviation is a strong player in the Navy's Manufacturing Technology programs. The Navy's Centers of Excellence (C.O.E.) focus principally on the Navy's specific needs and requirements. Activities at the Navy's Center of Excellence for Composites Manufacturing Technology and the Metalworking Center of Excellence provide critical technologies essential to meeting naval aviation air vehicle requirements. These initiatives, along with the Navy's Science and Technology Program, are developing a broad range of critical technologies for future naval aviation applications including: advanced fiber placement technology, resin transfer molding, process simulation and modeling, affordable signature control, energy dissipation and multiaxial materials characterization and design methodologies, unitized construction, primary structure adhesive bond integrity, effects of defects charactrization, toughened non-MDA polyimides, and corrosion resistant elevated

temperature polymers. A new effort is underway to improve our understanding of the behavior of composites in structures, evaluate commercially available alternate materials, and develop rational substitution methodologies and strategies for second sourcing which will reduce program risks and costs.

Our programs in air vehicle metals technologies focus on improving the performance of Navy components in the maritime environment as well as affordability. Ongoing efforts include: high strength and corrosion resistant steels, high speed machining, intelligent hot isostatic pressing of advanced alloys, advanced large scale casting of titanium alloys, and light weight hybrid materials such as Aluminum-Beryllium, Aluminum-Lithium and Aluminum - Molybdenum, Significant progress has been made toward these efforts that is anticipated to have a major impact on our next generation systems.

In air vehicle non-structural materials, a broad range of diverse activities are taking place. Advanced coating technologies which minimize the hazardous waste stream and effluents, yet retain performance and corrosion prevention requirements are in the process of development and transition. Programs such as nonchrome primers, waterborne topcoats, self-priming topcoats and reduced toxicity corrosion inhibiting compounds are at the leading edge of environmentally compliant naval aviation finishing systems. Electrically conducting, corrosion inhibiting sealants with elevated temperature capability and compliant with environmental regulations are also being evaluated.

From a supportability perspective, critical efforts in aircraft paint stripping including flash lamp and non-chloride strippers, low or no V.O.C. cleaners, primers, topcoats and corrosion preventative compounds, touch-up pens, ambient storable repair adhesives, composite heat damage evaluation, advanced composite repair, improved nondestructive evaluation technologies, corrosion fatigue, and corrosion detection via remotely queried sensors will be critical to obtain affordable, condition-based maintenance support.

3.1.2 *Propulsion*   Naval aviation advanced propulsion technologies are being developed under three principal programs: the Integrated High Performance Turbine Engine Technology Program, the Navy's C.O.E. for Metalworking Technology, and the Navy's 6.2 Propulsion Task. The focus is on the enabling technologies which address the unique concerns of the naval aviation propulsion community, specifically performance and affordability in the Navy's operational scenario. The critical technologies under development include: oxidation and hot corrosion resistant ceramic matrix composites, intermetallic high pressure turbine technologies, low sulfur nickel-based superalloys, advanced thermal barrier coatings, gamma-titanium aluminides, orthorhombic titanium aluminides, advanced single crystal processing and environmental effects characterization. Efforts are also underway to develop high temperature, non-MDA polymer composites for a variety of applications. These polymers must be durable in the Navy's environment, and offer performance, weight, and affordability benefits over current approaches.

Propulsion supportability efforts offer significant opportunities for affordability enhancements including: turbine blade and vane repair, non-proprietary thermal barrier coatings, and environmentally compliant engine wash procedures.

3.1.3 *Electronics & Sensors*   Electronics and sensors play a mission essential role in naval aviation systems. Advanced materials and processes provide the basis for many of the advancements in this area. Materials must be durable, perform at required levels and be cost effective for all-weather, day or night operations in the Navy's harsh maritime environment. The performance of radomes, windows, antennas and electrical systems can make a significant

difference in operational effectiveness. Electronics and sensor system level challenges include: transmission/reception efficiency, high power transmission, heat generation and dissipation, electromagnetic interference shielding, size and weight, corrosion resistance, and durability. To meet these challenges, the Naval Aviation Materials Competency is involved in a number of activities including: durable infrared missile domes, low dielectric and higher temperature radome materials, advanced composite enclosures and connectors, aluminum-beryllium assemblies, laser interferometry for piezoelectric sensors, and advanced thermal management materials including diamond and high thermal conductivity fibers.

4.0   MANAGEMENT AND EXECUTION

To effectively manage the broad range of technical activities to meet this complex set of requirements, the Naval Aviation Materials Competency has put into place a number of organizational and management initiatives. As part of the Base Realignment and Closure Commission decisions, the Naval Air Systems Command Headquarters and the Naval Air Warfare Center - Aircraft Division are consolidating at Patuxent River, MD. In October 1995, the Naval Air Systems TEAM took the initial step of standing up the new Aerospace Materials Division. This action co-locates and integrates materials and processes research, development, engineering and fleet support functions within a single entity. This co-location provides many mutual benefits to the Aerospace Materials Division and the Patuxent River Naval Air Test Center.

Subsequently, the national Naval Air Systems TEAM Materials Competency was establishd via the Materials Management Board (MMB). The MMB is chaired by the NAWC-AD Aerospace Materials Division. This activity integrates the resources, capabilities and authority of NAWC-AD Aerospace Materials Division in Patuxent River with the NAWC-WD China Lake and the three Naval Aviation Depots including Cherry Point, Jacksonville, and North Island Materials Competencies.

The Materials Competency is responsible for the full spectrum, life cycle materials research, development, test, evaluation, acquisition, engineering and fleet support for naval aviation air vehicles, propulsion, weapons, avionics and sensors. The emphasis of the MMB is to promote and facilitate the improved and more efficient use of resources and equipment, definition of technology requirements, enhanced technology transition, and establishes consistent engineering and technology policies and procedures throughout the TEAM. Naval Air System TEAM Materials Competency resources are assigned to programs and projects via Integrated Product Teams (IPT), Externally Directed Teams (EDT), or Enterprise Teams (ET). These assignments provide an enhanced focus on products by incorporating a direct-support business operating environment. The Competencies themselves are directly responsible for the allocation of critical resources, technical and managerial policies, processes, and strategic planning to meet naval aviation requirements. Engineers are empowered by the Competencies to provide representation on assigned teams. These assignments are essential to supporting the technical requirements during program execution in a downsizing, declining budgetary and acquisition reform environment.

5.0 CONCLUSION

The Naval Air Systems Material Competency is taking aggressive action to meet today's challenging and complex requirements. The integration of Materials Science and Technology, Acquisition Development and Production, and In-Service Support functions combined with the national Materials Competency resources will provide effective program support services and the efficent transition of Materials Competency products to the Naval Aviation TEAM, now and into the future.
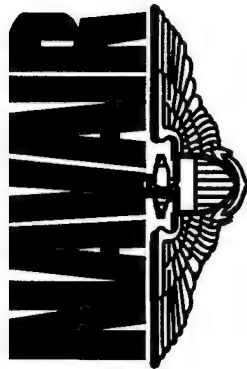
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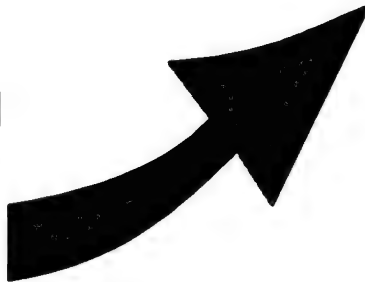## ADVANCED MATERIALS REQUIREMENTS, PROGRAMS AND INITIATIVES

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Aerospace Materials Division
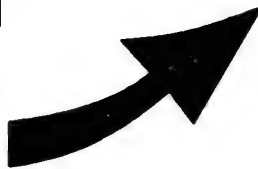*Naval Air Systems Team*
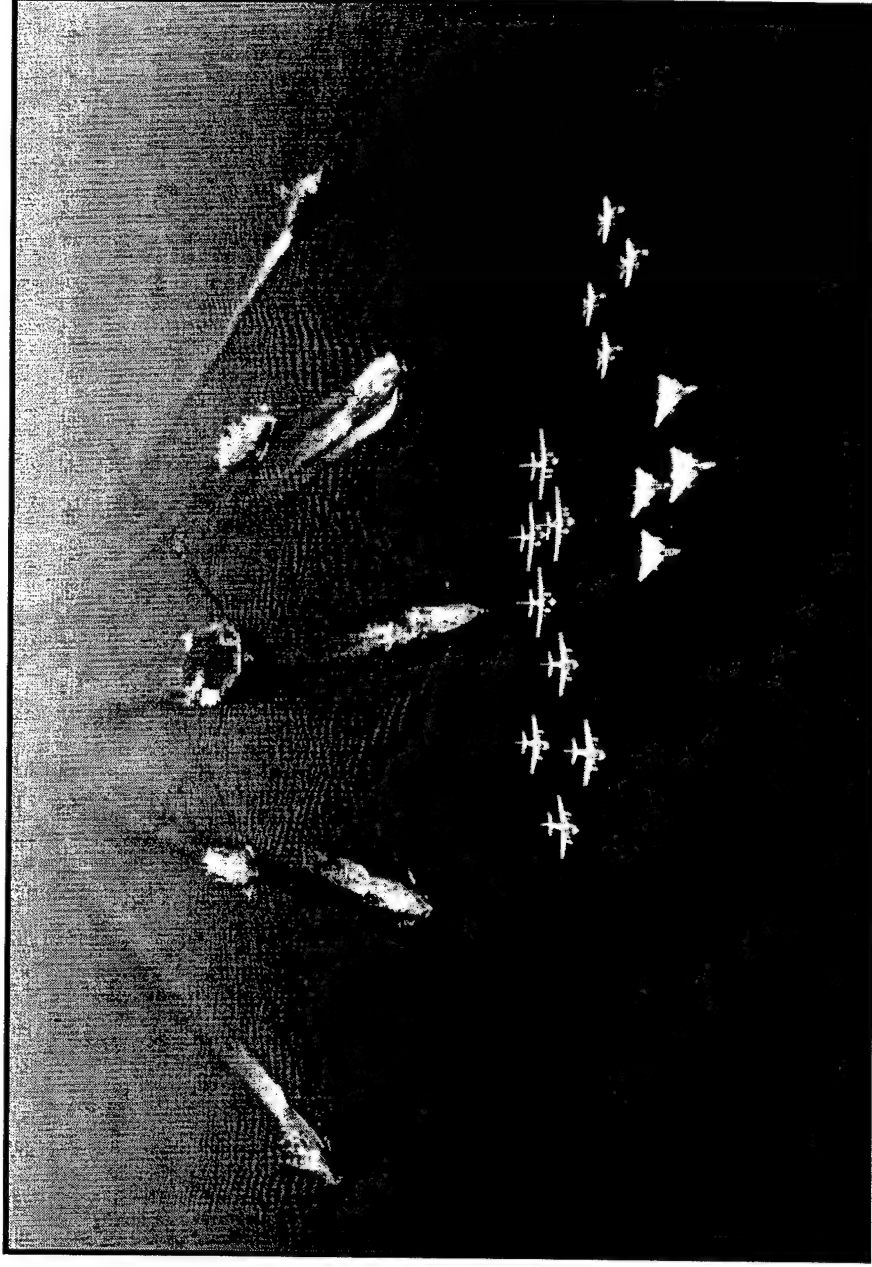
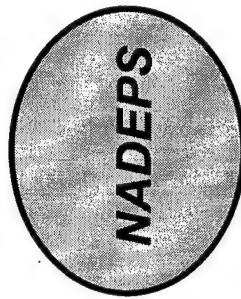NAVAL AVIATION SYSTEMS TEAM

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NADEPS

[MATERIALS DIVISIONS]

[MATERIALS]

NAWC
NAVAL AIR WARFARE CENTER
Aircraft Division

[AEROSPACE MATERIALS DIVISION]

NAVAIR

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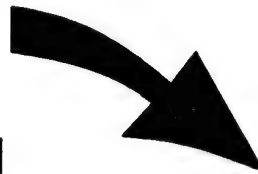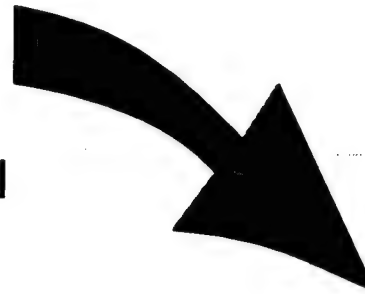
NAVAL AVIATION SYSTEMS

TEAM

MATERIALS
COMPETENCY MISSION

The materials competency encompasses the full spectrum, life cycle materials RDT&E, acquisition, engineering, and fleet support for naval aviation:

- Air Vehicles
- Avionics and Sensors
- Propulsion
- Weapons

NATIONAL NAVAL AVIATION MATERIALS COMPETENCY
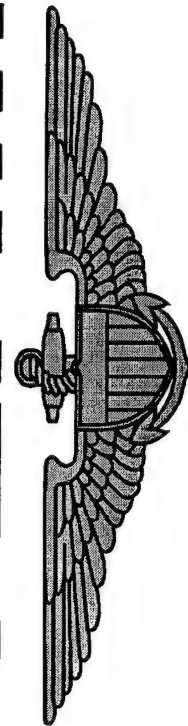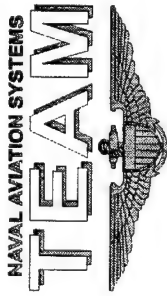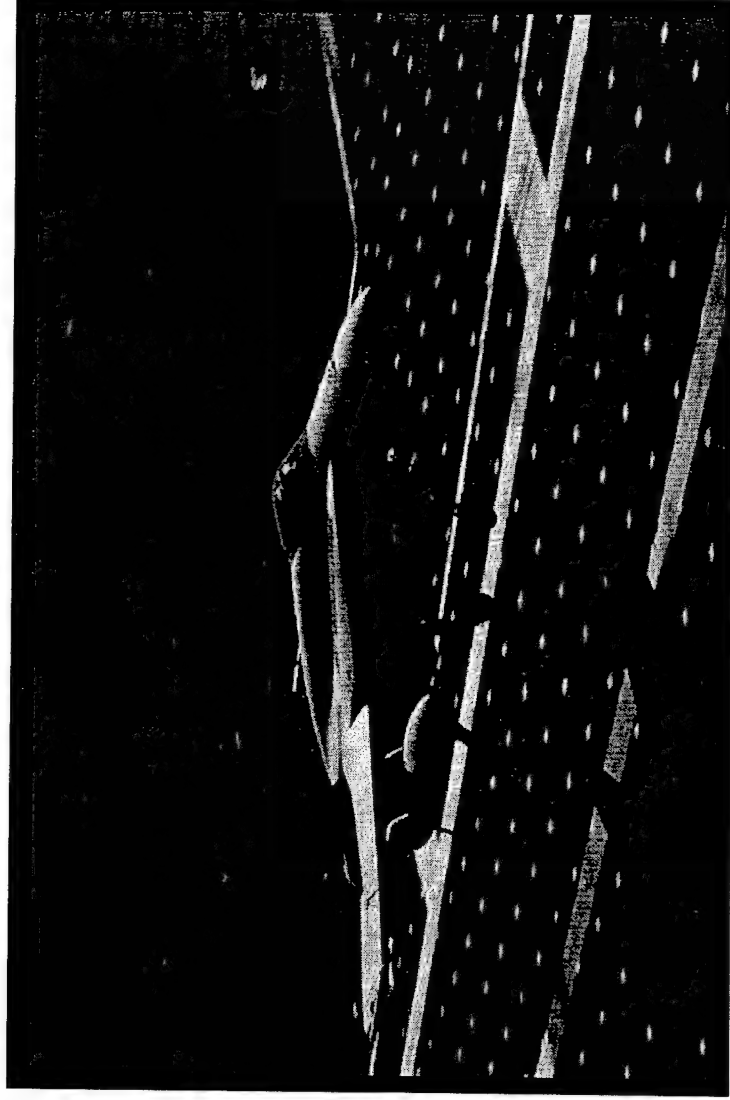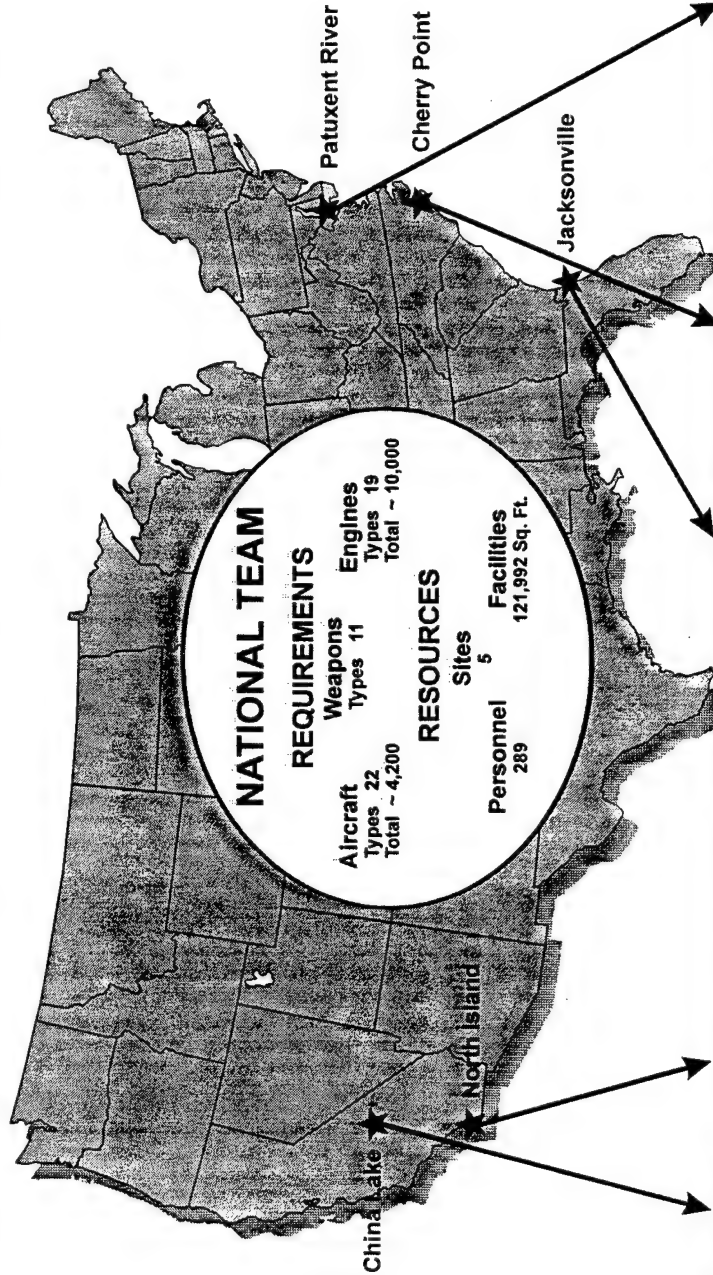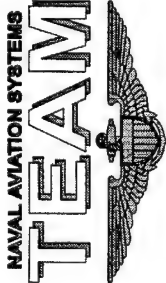
NAVAL AVIATION SYSTEMS TEAM

Patuxent River

Cherry Point

Jacksonville

China Lake

North Island

NATIONAL TEAM

REQUIREMENTS

Aircraft	Weapons	Engines
Types 22	Types 11	Types 19
Total ~ 4,200		Total ~ 10,000

RESOURCES

Sites	5	
Personnel	289	
Facilities		121,992 Sq. Ft.

NAWCWD CHINA LAKE

PRINCIPAL MISSION - Weapons RDT&E, Acquisition Development and Certification

PRINCIPAL PROGRAMS
- 6.1
- 6.2
- 6.4
- MANTECH
- CRADAS
- Cruise Missile
- SLAM-ER
- Harpoon,
- AIM-9X
- Standard Missile
- Sparrow
- RAM
- AM-RAAM
- JSOW, JDAM, JSAM

LAB SQ. FT. - 20,000

PERSONNEL - 42

NADEP NORTH ISLAND

PRINCIPAL MISSION - In-Service Engineering

COGNIZANT FIELD ACTIVITY
- Aircraft: - F/A-18, E2/C2, S-3, T-34, F-5
- Engines: - LM 2500 (Ship)
- LMTCs: - Preservation
  - Corrosion Control
  - NDI
  - Bearings
  - Adhesives
  - Tires
  - Heat Damage Evaluation
  - Heat Treatment
  - Welding
  - Transparencies

LAB SQ. FT. - 27,060

PERSONNEL - 51

NADEP JACKSONVILLE

PRINCIPAL MISSION - In-Service Engineering

COGNIZANT FIELD ACTIVITY
- Aircraft: - F-14, EA-6B, E-6, T-45, P-3, A-7 (FMS), T-2
- Engines: - F404, F414, TF-34, T-56, J52, J85, TF30, F110
- LMTCs - Environment
  - Thermal Spray
  - Testing
  - Organic Coatings
  - Tribology

LAB SQ. FT. - 19,000

PERSONNEL - 56

NADEP CHERRY POINT

PRINCIPAL MISSION - In-Service Engineering

COGNIZANT FIELD ACTIVITY
- Aircraft - H-1, H-46, H-53/H-3, H-60/H-2, AV-8B, C-130, F-4, V-22
- Engines - T58, T64, T700, T400, T406, F402, F405, J79
- LMTCs - Av. Gas Free Engr.
  - Composite Repair
  - Elastomeric Materials
  - Engine Blade/Vane Repair
  - Failure Analysis
  - Fluid Contamination
  - Inorganic Coatings
  - Vibration Analysis

LAB SQ. FT. - 11,932

PERSONNEL - 40

NAWCAD PATUXENT RIVER

PRINCIPAL MISSION - Aircraft RDT&E, Acquisition Development and Certification

PRINCIPAL PROGRAMS
- 6.1
- 6.2
- 6.3 (SERDP)
- 6.4
- MANTECH
- F-18 E/F
- V-22
- H-1 Upgrade
- JSF
- CSA

LAB SQ. FT. - 44,000

PERSONNEL - 100

DLM-01-15

NAVAL AVIATION SYSTEMS

TEAM

AEROSPACE MATERIALS TECHNOLOGY FOR NAVAL AVIATION NEEDS

A FULL SPECTRUM APPROACH
S&T, ACQUISITION AND MAINTENANCE NEEDS
ARE FULLY INTEGRATED FOR ALL AIRCRAFT SYSTEMS

ACQUISITION SUPPORT/ RISK ASSESSMENT

- Requirements Definition
- Source Selection Design Review
- Programmatic Risk
- Award/Performance Monitoring
- Materials & Processes Certification
- Transition Materials
- Provide/Verify Design Allowables
- Mil-Handbooks/Specs

FLEET SUPPORT/AIRCRAFT MAINTENANCE

- Hazardous Waste Minimization/Environmental Compatibility Program
- Aircraft & Engine Maintenance/Repair/Life Extension Technology
- Failure Analysis
- Transition Improved Maintenance Materials & Operational Chemicals to the Navy Maintenance Community
- Materials Deterioration Program
- Develop/Revise Maintenance Manuals

MATERIALS SCIENCE AND TECHNOLOGY

- Metals & Ceramics
- Propulsion Materials
- Avionics
- Corrosion Technology/ Materials Protection
- Advanced Polymers & Composites
- Functional Materials
- Energetics
- Nondestructive Evaluation
- Countermeasure Materials
- SBIRs
- Manufacturing Technology

MATERIAL AND PROCESS PROGRAMS AND INITIATIVES

NAVAL AVIATION SYSTEMS TEAM

Technical Coordination

- Acquisition Environmental Product Support Team
- Navy Manufacturing Technology Centers of Excellence
- Naval Aviation Science & Technology Office
- Naval Aviation Materials Competency
- Joint Service Activity
- Navy Council on Materials and Structures
- Lead Maintenance Technology Centers

NAVAL AVIATION SYSTEMS TEAM
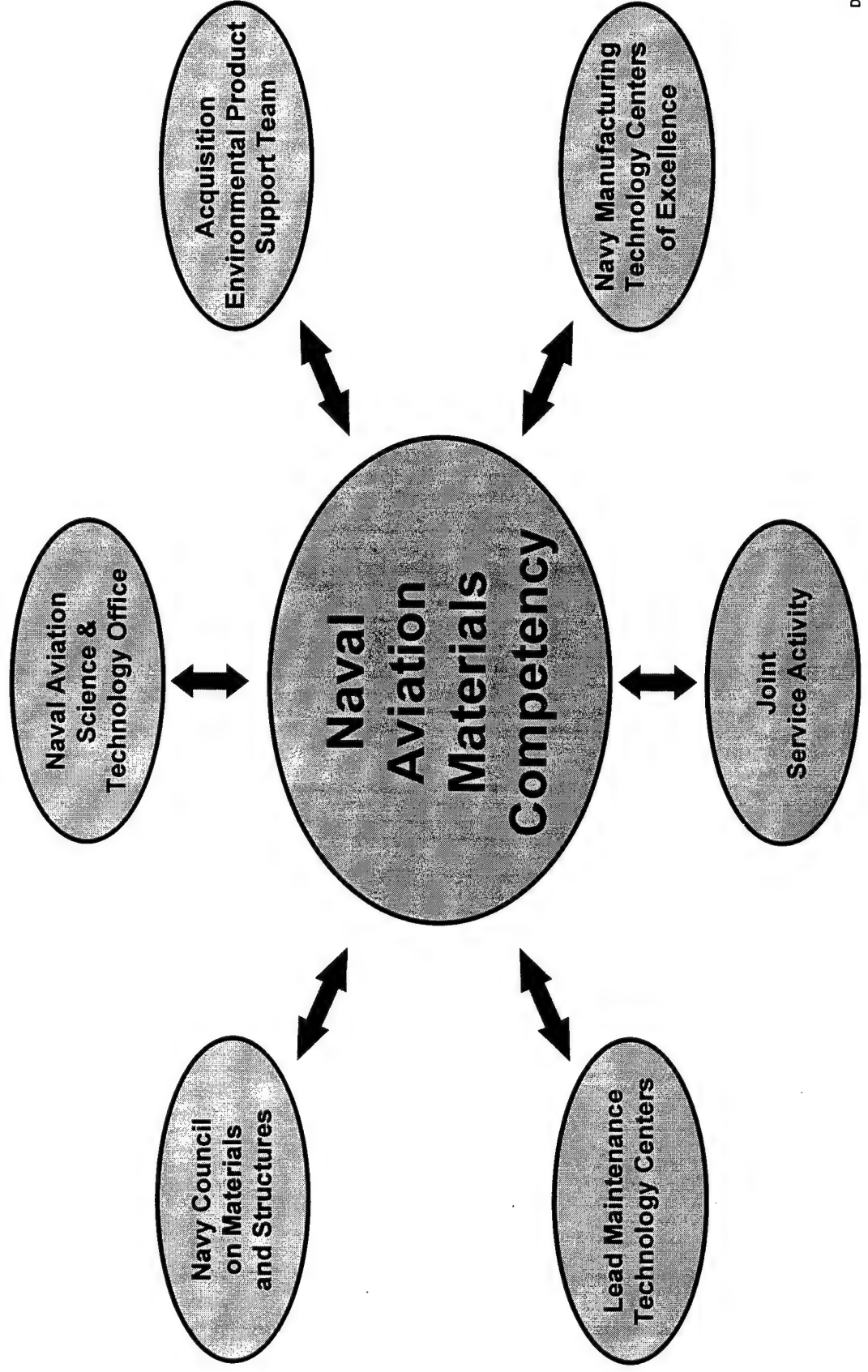
CURRENT TRENDS & SITUATIONAL ASSESSMENT

- **Resources Declining Across-the-Board**
  - **Science & Technology**
    - **Research and development foundation to meet the requirements of advanced systems**
  - **Acquisition Development**
    - **Cost, schedule and performance risk reduction**
    - **Affordable production initiatives**
  - **Systems Procurement**
    - **Replacement/upgrade of fleet assets**
  - **Systems Maintenance And Support**
    - **Maintain fleet safety affordably**

NAVAL AVIATION SYSTEMS
TEAM

CURRENT TRENDS &
SITUATIONAL ASSESSMENT (cont.)

- Increasingly Complex Set of Emerging Technical Requirements

  - Enhanced mission effectiveness/performance

  - Multi-service/multi-mission (inc. ASTOVL)

  - All-weather, day and night capable

  - Environmental and safety

  - Stealth

  - EMI protection

  - Live fire capable

  - Condition-based maintenance

NAVAL AVIATION SYSTEMS
TEAM

STRATEGY

Develop a series of strategies designed to meet the challenge by:

- Effectively integrating and focusing S&T, acquisition engineering, and in-service support programs and resources

- Streamlining advanced technology transition and certification

- Facilitating the formation of collaborative partnerships with the joint services, other government activities, and industry to better leverage and focus available resources

- Addressing affordability as an integral component in all of our activities
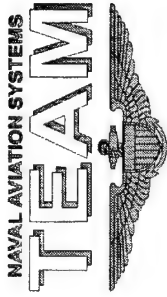
NAVY UNIQUE
AIRCRAFT REQUIREMENTS

Navy ship-based aircraft have to do everything that land based aircraft do, but in a more hostile environment and under more adverse conditions.

Carrier aviation operational constraints:

- Limited space for takeoff and landing
- Catapult and arresting gear
- Maritime environment
- Maintenance support
- Multi-mission platforms
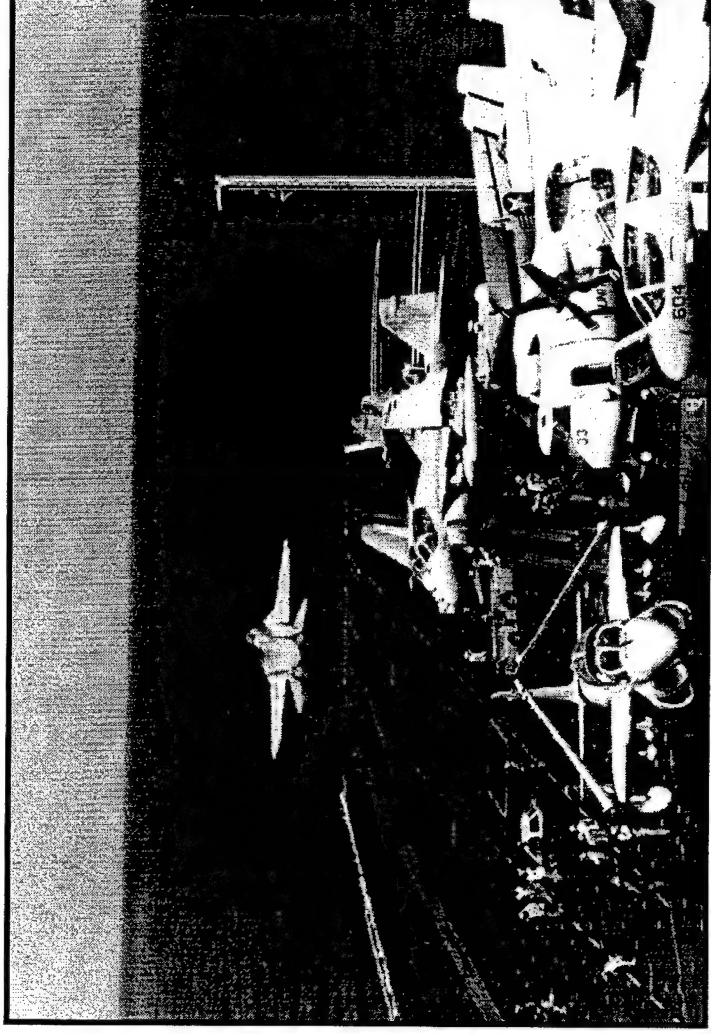
LIMITED LAUNCH AND RECOVERY SPACE

NAVAL AVIATION SYSTEMS
TEAM

Typical Runway

- Length - 10,000'
- Width - 300'

USS Nimitz (CVN-68)
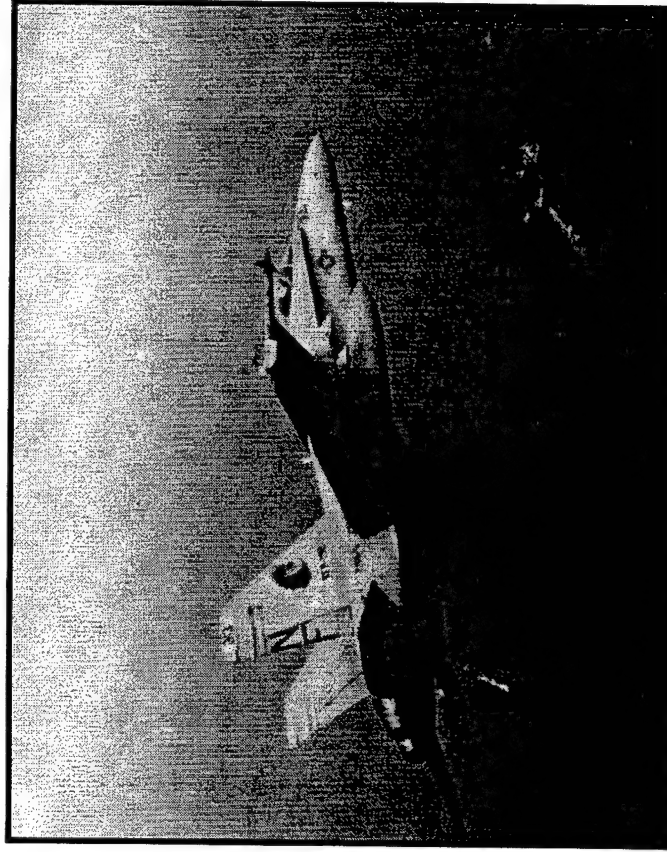
- Flight Deck Length - 1,092'
- Flight Deck Width - 250'
- Recovery Area - 780' X 120'
- Launch Area - 390' X 120'

NAVAL AVIATION SYSTEMS
TEAM
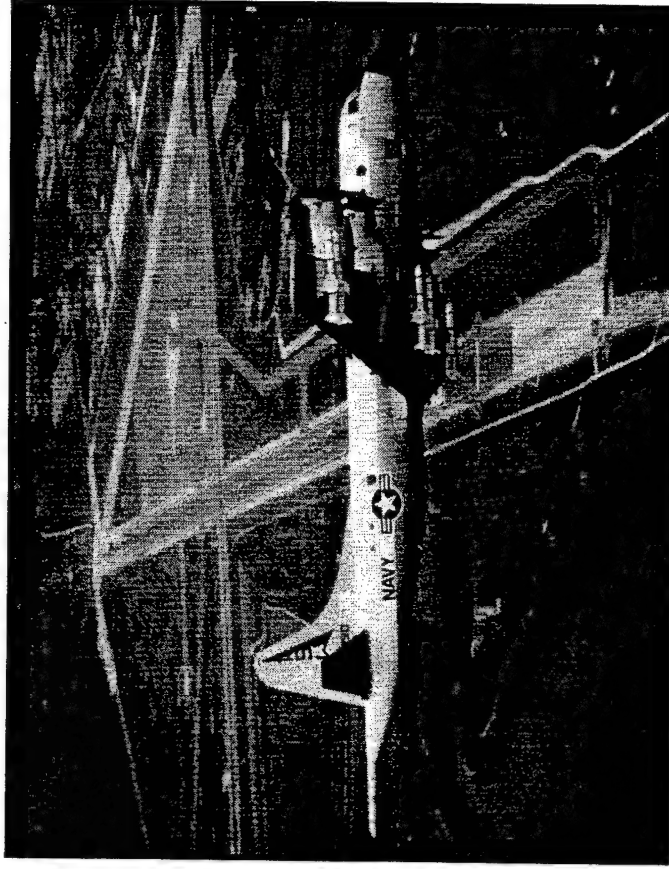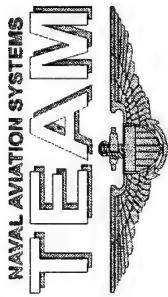
CARRIER AIRCRAFT LAUNCH AND RECOVERY REQUIREMENTS

- Structural design must be lightweight, yet meet fatigue life criteria for catapult takeoffs, arrested landings and high sink-rate touch-and-gos
- Engine response must be rapid and precise for altitude and airspeed control on the glide slope as well as acceleration to full power for wave-off or bolter
- Landing gear must have greater strength and built-in tow and holdback fittings
- Wing high-lift devices are needed to allow safe low speed flight
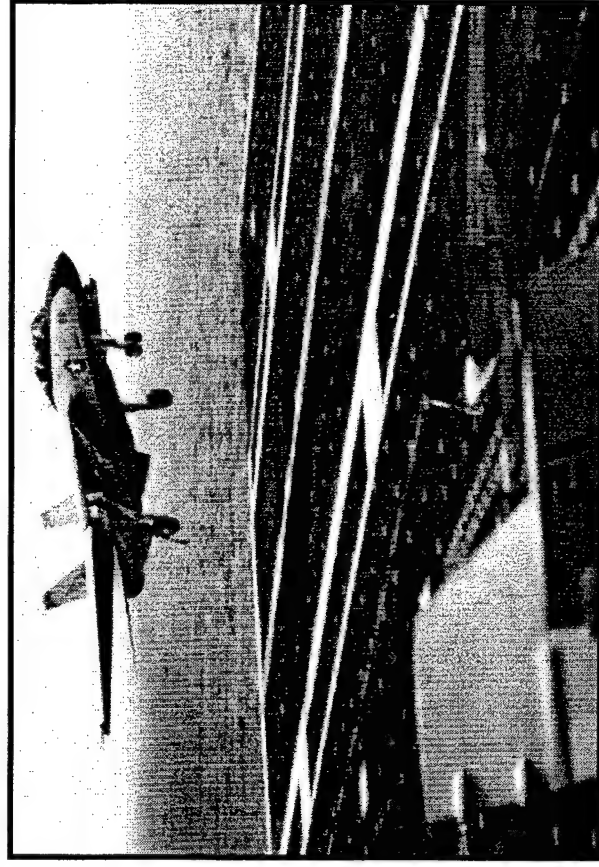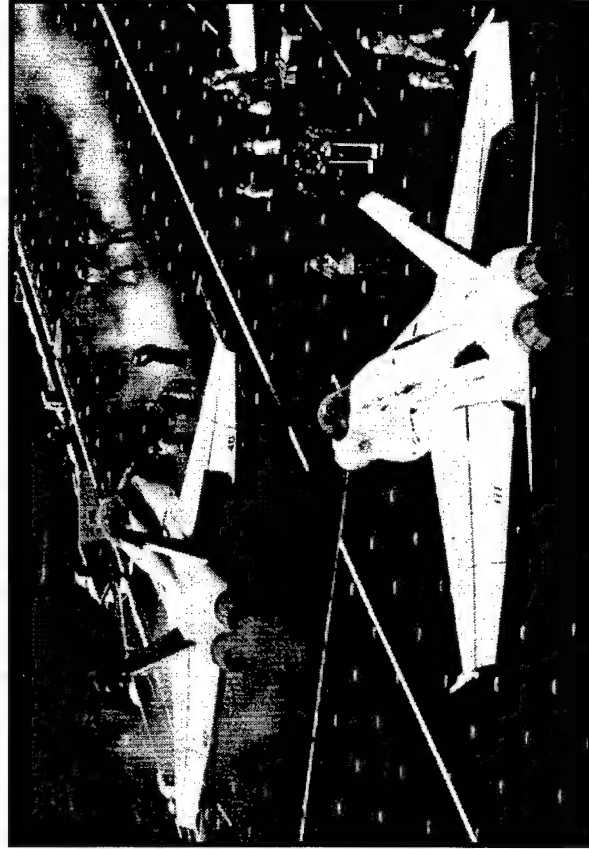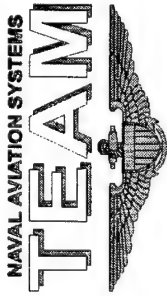
HARSH, CORROSIVE ENVIRONMENT

NAVAL AVIATION SYSTEMS TEAM

The maritime environment directly impacts every material and process selection for the Navy's advanced systems
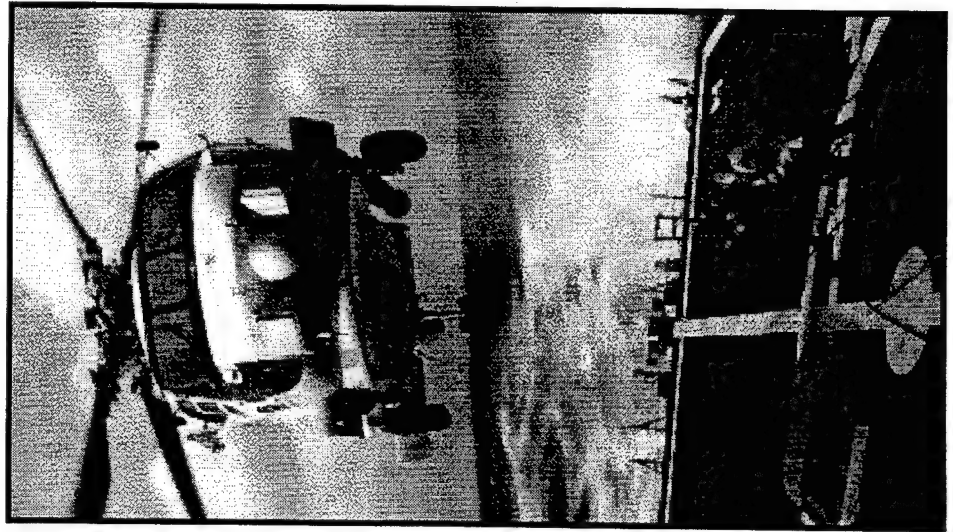
- Salt air
- High humidity
- High and cryogenic temperatures

- Stack gases/ engine exhaust
- White water
- Steam

MAINTENANCE CONSTRAINTS

Flight Deck

- Line maintenance performed in open air environment
- Limited deck space dictates common support equipment/ built-in test

- Corrosive environment
- Limited freshwater for wash-down

- Crowded conditions
- Rolling/pitching deck

MAINTENANCE CONSTRAINTS

Hangar Deck

- Limited storage space dictates requirement for common spares and support equipment
- Restocking at sea requires underway replenishment when out of C-2 range
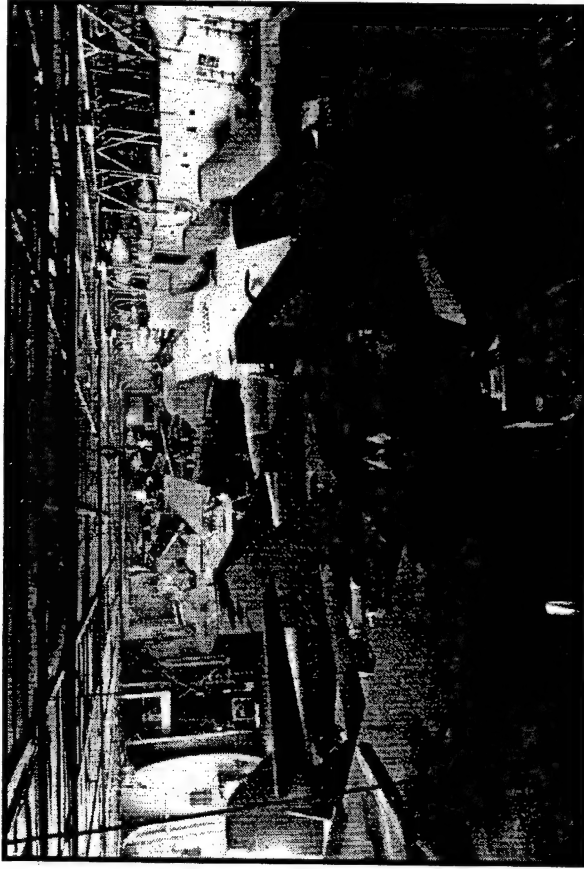
- Limited space for intermediate maintenance
- Rolling/pitching deck
- Engines must be removable without cranes, with wings folded

DLM-01-32

MATERIALS AND PROCESSES APPLICATIONS

NAVAL AVIATION SYSTEMS TEAM

AIRFRAMES

High Speed Machining for Aluminum Alloys

Electromagnetic Interference/ Lightning Source Abatement

Fast Cure Lightweight Sealants

Environmentally Compliant Coatings, Cleaners and Corrosion Prevention Materials

Composite Repair Materials and Procedures
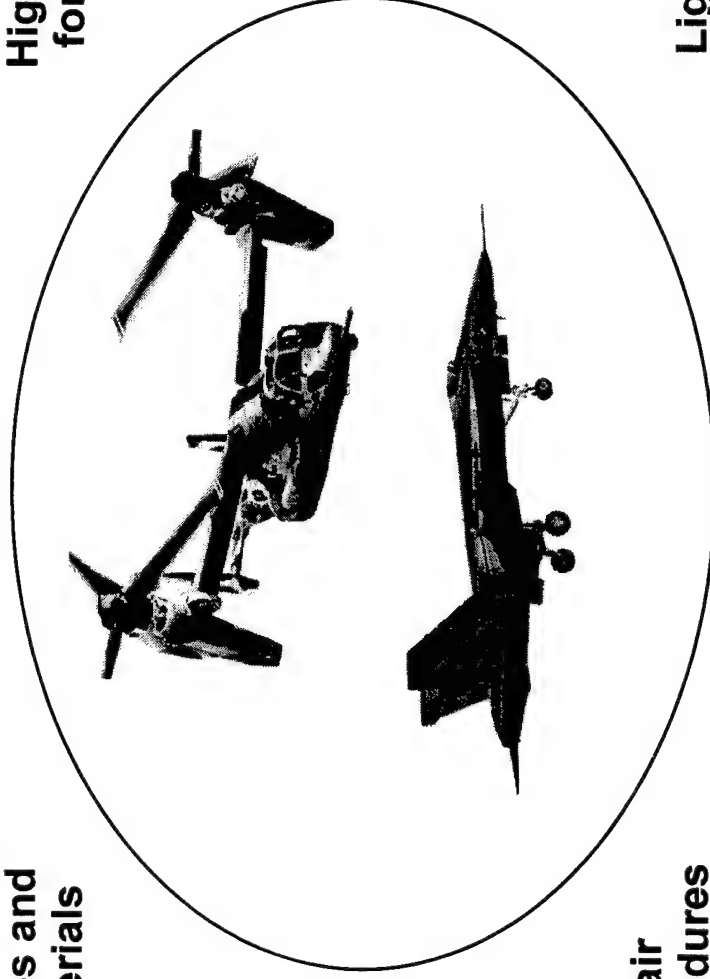
Advanced Fiber Placement/ Automated Tape Lay-up

S.O.T.A. Composites and Landing Gear Materials

NAVAL AVIATION SYSTEMS TEAM

MATERIALS AND PROCESSES APPLICATIONS

ENGINES

CMC Flaps and Seals

M50 NIL Material

Single Crystal HPT
Blades and Vanes

Thin Density
Chrome Bearings

Ceramic Shrouds

TBC Blades/Vanes

Composite Front Frame

DLM-01-34

MATERIALS AND PROCESSES APPLICATIONS

NAVAL AVIATION SYSTEMS
TEAM

WEAPONS

Advanced Energetic Materials
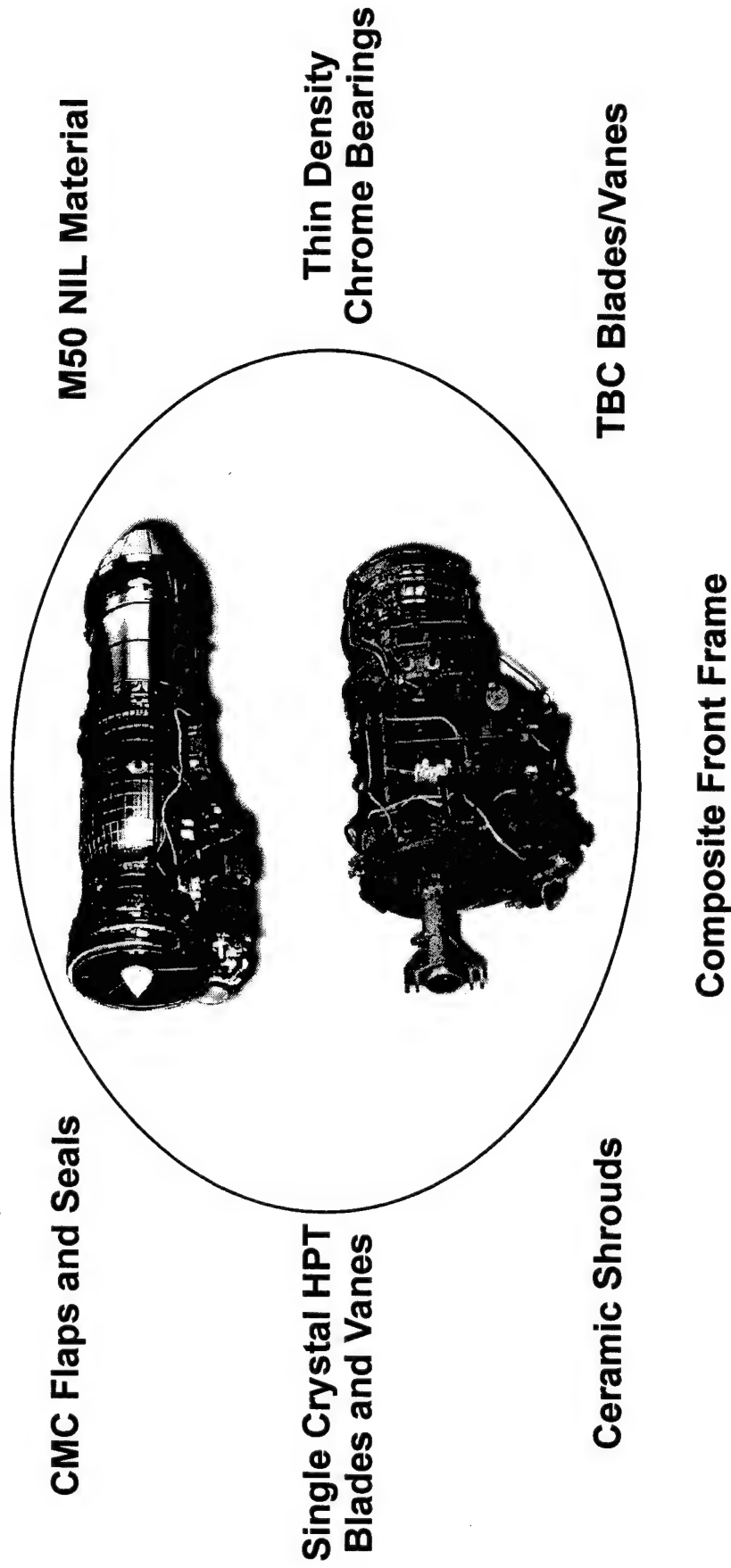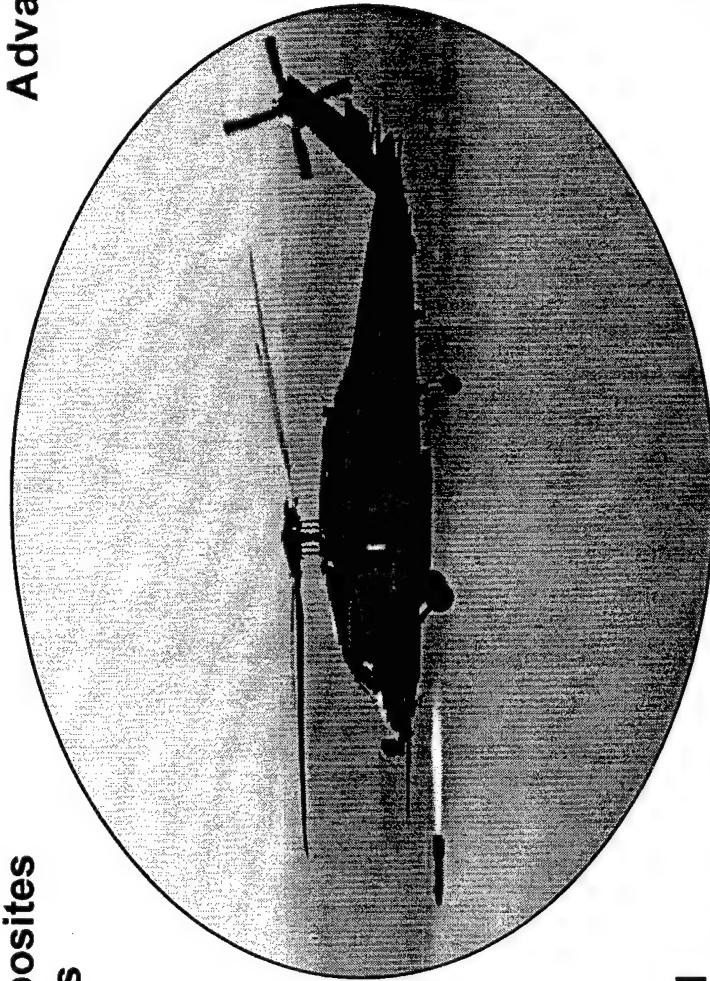
Lightweight Components

Low Cost Turbine Components

Low Cost Composites and Metals

Diamond Domes/Films

Advanced Transmissive Materials

DLM-01-35

AIR VEHICLE INITIATIVES

Composites

GOALS

- Optimized affordability and performance
  - Highly tailored designs
  - Advanced Composites
  - Automated processes
  - Flight certifiable
- Second Sourcing
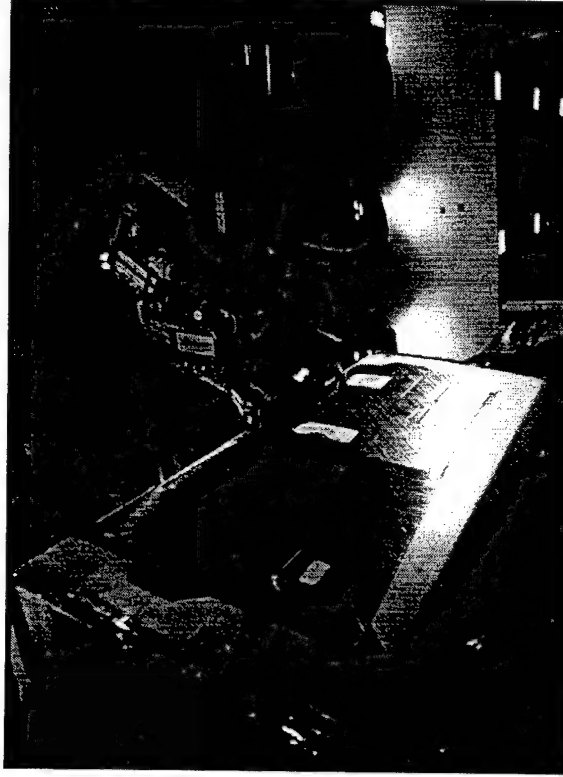
PROGRAMS

- Navy Science & Technology Program
- C.O.E. for Composite Manufacturing Technology
- Joint Air Force/Navy Composite Affordability Initiative (CAI)
  - JSF Technology Transition
  - Fast Track Demonstration
  - Pervasive Technologies

CRITICAL TECHNOLOGIES

- Advanced fiber placement
- Resin transfer molding
- Process simulation and modeling
- Affordable signature control
- Toughened non-MDA polyimides
- Unitized construction
- Adhesive bonding
- Energy dissipation and multiaxial materials characterization
- NDE for complex/thick composites

AIR VEHICLE INITIATIVES

Metals Technologies

GOALS

- Affordability
- Lighter weight
- Corrosion resistant
- Near net shape processing
- Higher strength
- Damage tolerant

CRITICAL TECHNOLOGIES

- High strength/corrosion resistant steels
- High speed machining
- Intelligent hot isostatic pressing of advanced alloys
- Rapid solidification
- Advanced large scale casting of titanium alloys
- Lightweight materials (e.g. aluminum-beryllium)
- Nano-structures

NAVAL AVIATION SYSTEMS
TEAM

AIR VEHICLE INITIATIVES

Non-Structural Materials Technologies

GOALS

- Develop advanced coating technologies that retain performance while minimizing pollution and hazardous waste

UNICOAT (TT-P-2756)

EPOXY TOPCOAT (MIL-C-22750)
LOW VOC PRIMERS (MIL-P-85582, MIL-P-23377, TT-P-2760)

UNICOAT FOR STEEL
WATER-BORNE TOPCOAT

WATER-BORNE UNICOAT

ZERO VOC TOPCOAT

ZERO VOC PRIMER

ZERO VOC UNICOAT

1992   1994   1996   1998   2000   2002   2004
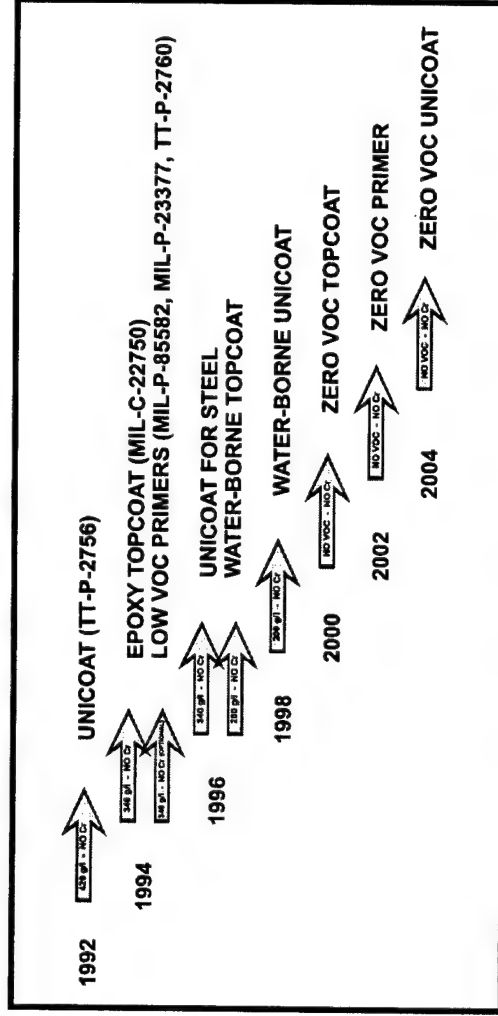
CRITICAL TECHNOLOGIES

- Nonchrome primers
- Waterborne topcoats
- Self-priming topcoats
- Reduced toxicity corrosion inhibiting compounds
- Electrically conducting, corrosion inhibiting, environmentally friendly sealants with high temperature capability

NAVAL AVIATION SYSTEMS TEAM

AIR VEHICLE INITIATIVES

Supportability Technologies

GOALS

- Develop lower cost, environmentally compliant paint stripping materials and processes
- Extend the shelf life of repair adhesives
- Enhance condition-based maintenance methodologies
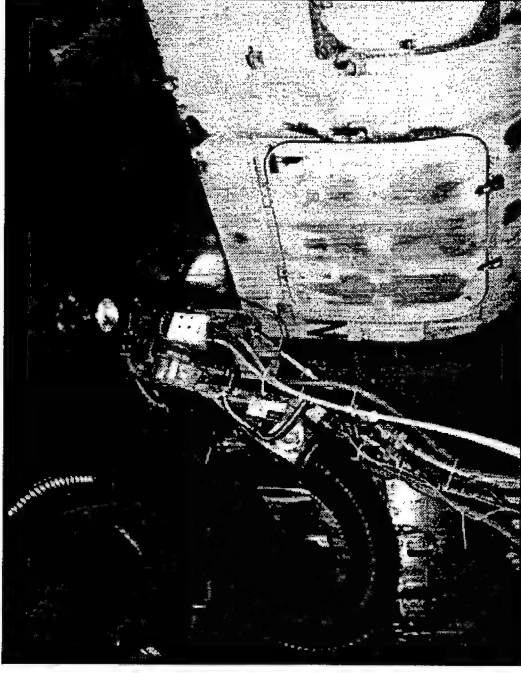
CRITICAL TECHNOLOGIES

- FLASHJET® and non-chloride paint strippers
- Low or no VOC-cleaners, primers, topcoats, and corrosion preventative compounds
- Touch-up pens

- Composite heat damage evaluation
- Advanced composite repair
- Improved nondestructive evaluation
- Remote sensing of corrosion and corrosion fatigue
- Signature control supportability

NAVAL AVIATION SYSTEMS
TEAM

PROPULSION INITIATIVES

GOALS

- Durability in Navy environment
- Increased use of high strength, lightweight materials and structures
- Large single-piece cast gamma-titanium structure
- Higher temperature materials
- Reduce blade and vane repair costs
- Condition-based maintenance
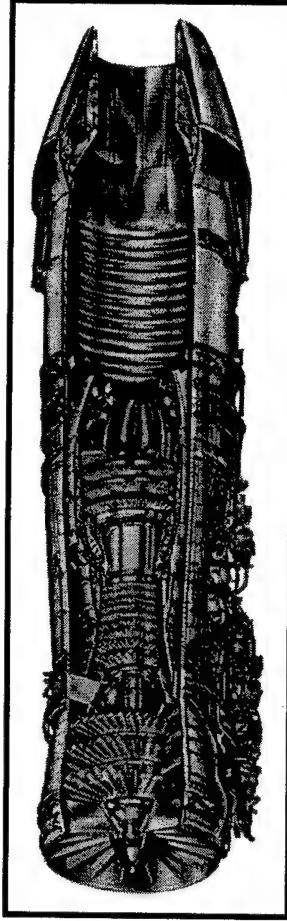
PRINCIPAL PROGRAMS

- Integrated High Performance Turbine Engine Technology (IHPTET)
- Center of Excellence for Metalworking Technology
- Navy 6.2 Engine Technology

CRITICAL TECHNOLOGIES

- Oxidation/hot corrosion resistant CMC
- Advanced high temperature disk materials
- Intermetallic high pressure turbines
- Environmental effects characterization
- Low sulfur nickel-based superalloys
- Advanced blade/vane repair
- Advanced thermal barrier coatings
- Thermal spray coating removal
- Gamma-titanium aluminides
- In-situ HT composite alloys
- Orthorhombic titanium aluminides
- Enhanced nondestructive inspection
- Advanced single crystal processing

NAVAL AVIATION SYSTEMS
TEAM

ELECTRONICS AND SENSORS INITIATIVES

GOALS

- Increase transmission/reception efficiency
- Minimize size and weight
- Increase corrosive resistance
- Increase durability
- Improve thermal management
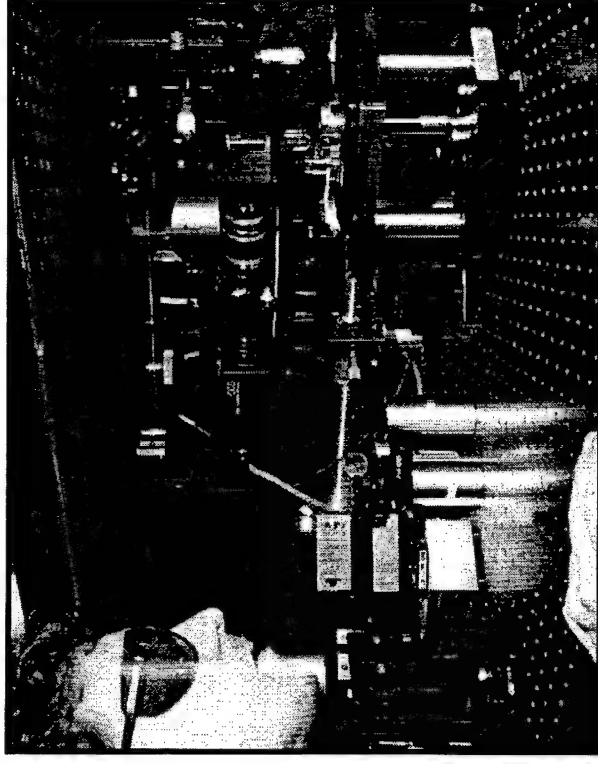
CRITICAL TECHNOLOGIES

- Durable infrared missile domes
- Low dielectric and higher temperature radome materials
- Advanced composite enclosures and connectors
- Multi-chip modules and MEMs
- Electro-optic and conductive polymers
- Aluminum-beryllium assemblies
- Laser interferometry for piezoelectric sensors
- Affordable diamond technology

FUTURE AIRCRAFT
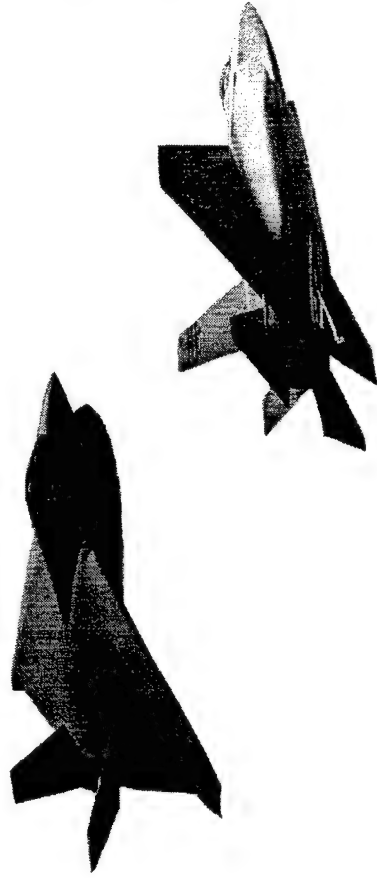
Joint Strike Fighter (JSF)

Service plans call for the JSF to replace the F-16 and A-10 and complement the F-22 in the Air Force, replace the AV-8B and F-18 in the Marine Corps, and provide the Navy with a stealthy first day strike aircraft to complement the F/A-18E/F. The focus of the JSF Program is on affordability-reducing development, production, and ownership cost.
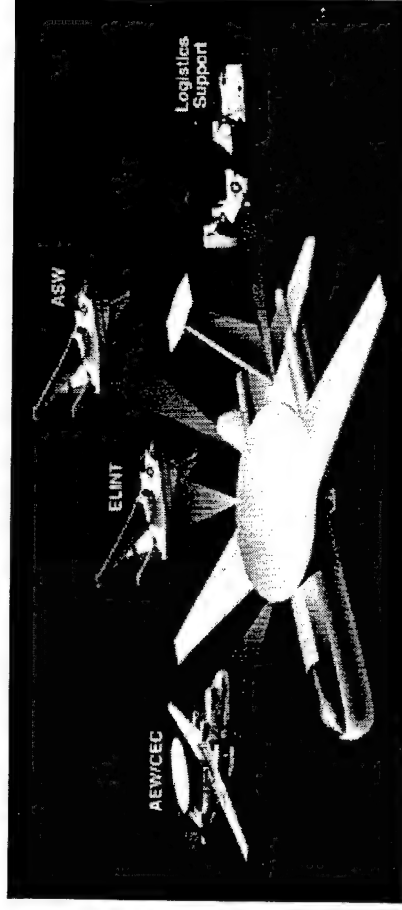
Common Support Aircraft (CSA)

Current naval mission support aircraft (S-3, E-2, ES-3, and C-2) will reach the end of their operational service lives between 2010 and 2015. A study is being made to examine the possibility of combining the mission functions now performed by these multiple platforms into a single aircraft (CSA).
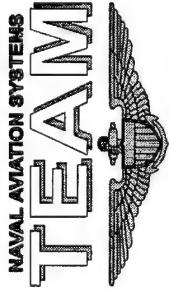
AIRCRAFT MATERIALS TECHNOLOGY PRODUCTS TO THE FLEET

NAVAL AVIATION SYSTEMS
TEAM

UNICOAT POLLUTION PREVENTION COATING TECHNOLOGY

LOW OBSERVABLE COMPOSITE FRONT FRAME STRUCTURE

FLEET & DEPOT REPAIR MATERIALS & PROCEDURES FOR ORGANIC COMPOSITES

LOW SULFUR COATINGS FOR GREATER DURABILITY OF ENGINE COMPONENTS

IMPROVED DURABILITY LANDING GEAR STEEL
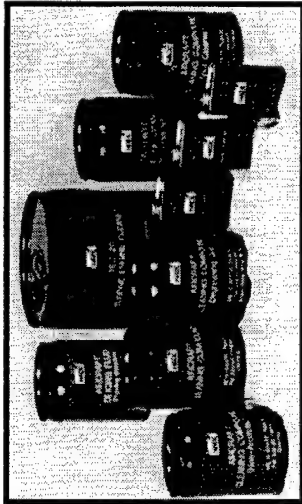
AIRCRAFT & ENGINE MAINTENANCE PRODUCTS & CORROSION PREVENTIVE MATERIALS & PROCEDURES
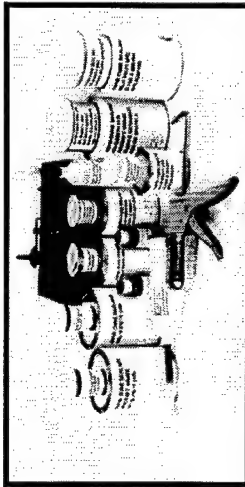
LIGHTWEIGHT, FAST CURING, HIGH PERFORMANCE SEALANTS

AV-8B Materials Usage
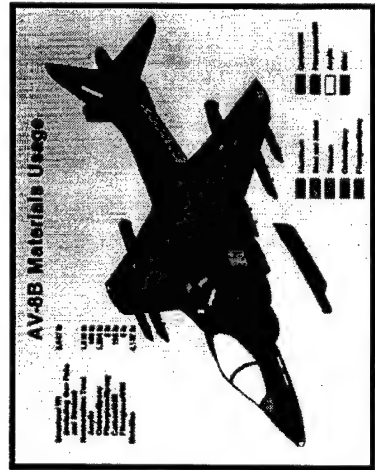
ADVANCED POLYMERIC COMPOSITES & HIGH STRENGTH/DURABLE ALUMINUM ALLOYS

DLM-01-41

ADVANCED PROPULSION MATERIAL DEVELOPMENT FOR NEXT GENERATION NAVY AIRCRAFT

Eui W. Lee, W. E. Frazier, G. London,
R. Mahapatra, R. Kowalik, and B. Pregger
Naval Air Warfare Center, Aircraft Division, Code 4.3.4
Patuxent River, MD 20670

ABSTRACT

To maintain the Navy's technological advantage in carrier based aircraft warfare mission, new improved capabilities are needed. Required improvements include expansion of the flight performance envelope, superior maneuverability, strike radius enhancement and durability. Additionally, dramatic reduction in military spending has imposed the need of affordability for new defense systems. To meet these needs, naval aviation systems require significant advances in gas turbine propulsion systems. One single most important requirement for the improved, durable and affordable engine is the development of high performance material and innovative material processing technology. One thrust of this area is in NAWCAD Patuxent River is to evaluate and understand the effect of the Navy operating environment on candidate high temperature materials used in propulsion systems and engine exhaust washed areas. These materials include high temperature coatings, ceramics, superalloys and intermetallics. In this paper, the Navy's effort on these materials in terms of development, evaluation, improvement and characterization will be described.

1. INTRODUCTION

The role of the Navy's propulsion materials science and technology (S&T) work is three pronged: (i) provide technical solutions to generic problems occurring in currently deployed propulsion systems, (ii) support the Navy's acquisition endeavors by providing the expertise and technology required to make the Navy a "Smart Buyer", and (iii) assure the development of the technology required to meet the needs of future propulsion systems. An integral part of the Navy's program is the emphasis given to providing reliable, sustainable and inspectable propulsion technology that is affordable.

In order to meet the performance goals of the IHPTET program, the exit temperature of the compressor (T3) will be 760 C. Currently, nickel-base superalloys are used in the aft stages of the compressor. To enhance engine performance, the use of lighter weight titanium alloys, and gamma and orthorhombic titanium aluminides is desirable. The

Navy's program on aligned microstructure of titanium aluminides is designed to address this issue.

Ceramic matrix composites (CMC's) are being aggressively pursued for military aircraft applications as both propulsion (turbine engine) materials and airframe structural materials in areas of the exhaust stream (e.g. nozzle and exhaust-washed structures). This pursuit is being driven by the need for faster and more mobile aircraft, missiles and ground-based weapons which are dependent upon higher thrust to weight propulsion systems. These higher powered propulsion systems will require higher operating temperatures which exceed the capabilities of existing superalloys.

The Naval Aviation Depots maintain and refurbish a wide variety of propulsion systems. Many of these use a NiAl coatings that reduces wear and extend blade life. Unfortunately, there are a wide variety of coatings and application processes required for use by the original equipment manufacturers. It is the intent of the Affordable Coatings Program to dramatically reduce the cost associated with coating air foils by reducing the number of processes and coating used.

2. DESIGN AND DEVELOPMENT OF DIRECTIONALLY SOLIDIFIED *ALIGNED IN-SITU* HIGH TEMPERATURE COMPOSITE ALLOYS (Ti-Al-Nb & Ti-Al-Mo) FOR ADVANCED PROPULSION SYSTEMS.

In this program we develop the directionally solidified (DS) *aligned in-situ* high temperature composites (Ti-Al-Nb and Ti-Al-Mo alloys) for advanced propulsion systems. Our objectives are: (1) to develop Ti-Al-Nb and Ti-Al-Mo *in-situ* composite alloys using the directional solidification method, (2) explore physical properties: i. e. yield strength, fracture toughness and creep strength, and (3) assess the microstructural stability under conditions of static and cyclic exposures at homologous temperatures of $0.85T_m$, $0.89T_m$ and $0.92T_m$ for these composites.

High temperature *in-situ* composites offer potential for significant improvements in operating temperature capability and strength level, compared to existing superalloys in the advanced gas turbine engine applications. Systems of interest include Ti-Al-Nb and Ti-Al-Mo based alloys (1-4). These alloys are expected to exhibit a lamellar and/or rod like morphologies. In rod-like structures, the rod morphologies may be circular, faceted or irregular in cross section. The key to acceptable performance is long-term microstructural stability at elevated temperature so that integrity of mechanical properties is assured. Service conditions that could promote/accelerate degradation are static exposure at high temperatures or thermal cycling (5).

Intrinsically, *in-situ* composites are stable at elevated temperatures, a characteristic derived from their solidification under near equilibrium conditions, coupled with the formation of low-energy interface boundaries (6). However, even in the absence of growth defects, coarsening can take place on prolonged static exposure at temperatures > $0.9 \ T_m$ by two-dimensional Ostwald ripening mechanism (7-9). The free energy of the system is reduced when a large lamellae grows at the expense of a smaller one. In thermal

cycling, microstructural instability may occur due to thermal expansion mismatch between constituents, allotropic transformation in the matrix, or a change in the mutual solubility of the eutectic phases with the temperature (5).

It has also been proposed theoretically and confirmed experimentally that coarsening is a sensitive function of and is accelerated by growth faults in the composite microstructure (8,10, 11). With a rod-like morphology, faulting can take the form of rod branching and rod termination. Cline (8) and Weatherly and Nakagawa (10, 11) have considered the mode and kinetics of coarsening involving fault migration and annihilation. Consequently, in the following section, we propose a detailed study of solidification behavior, mechanical properties, and the effects of isothermal and cyclic exposure at $T/T_m > 0.75$ on the strength and fracture toughness of Ti-Al-Nb and Ti-Al-Mo aligned composites.

TECHNICAL APPROACH:

The major thrusts of this research are as follows:
A). Preparation of *aligned in-situ* composites
The Ti-Al-Nb and Ti-Al-Mo alloy rods of 10mm were prepared by non-consumable electrode arc melting of high purity Niobium (99.998 at.%), Molybdenum (99.998 at.%), Aluminum (99.999 at.%) and titanium (99.998 at.%) under a purified argon atmosphere. The as-cast microstructure is composed of randomly oriented grains with lamellar or rod-like arrangements of eutectic and/or intermetallic phases in these eutectics. These cast rods were then remelted and unidirectionally solidified at an appropriate solidification rate to produce directionally *aligned in-situ* composite microstructure in these alloys. Optical and transmission electron micrographs of the aligned microstructure are shown in Figure 1 and Figure 2.
B). Heat treatment
The Ti-Al-Nb and Ti-Al-Mo aligned composites were annealed at 950^0C for approximately 24 hours obtain a fully homogeneous microstructure. The heat treatments was performed under pure argon atmosphere or in vacuum. After heat treatment, chemical analysis was performed to determine the compositions of the eutectics.
C). Mechanical Properties
A series of experiments on Ti-Al-Nb was performed. In the first set of experiments, the specimens with different grain sizes were prepared for compression testing. Annealing was done at temperatures from 1000 C to 1500 C to produce the unrecrystallized, duplex and the fully lamellar microstructures. Results indicate that successively higher temperature anneals produce increasing grain and colony sizes from 100µm in the unrecrystallized microstructure to 1000µm in the fully lamellar microstructure. The compression testing was performed at room temperature at a slow strain rate, using an Instron-type testing machine. The result is shown in Figure 3. A sequentially lower yield stress was produced on samples tested at increasingly higher temperatures for a given microstructure. Same type of the compression test will be performed on the Ti-Al-Nb and Ti-Al-Mo aligned composites. These results will provide dependence of yield strength on orientation of lamellar structure in these composites and therefore it will be possible to tailor a specific oriented microstructure for desired physical properties.
D). Thermal Stability Study

The directionally solidified rods of Ti-Al-Nb and Ti-Al-Mo aligned composite alloys will be cut into 25mm lengths, will be placed in alumina boats and will be subjected to isothermal exposure at 900^0C, 1000^0C and 1177^0C in flowing argon for times up to 25×10^5s. These temperatures correspond to homologous temperature of approximately 0.85, 0.89 and 0.92 respectively for these eutectics. At periodic intervals, a transverse slice of 3mm will be taken and the balance of the rod will be placed in the furnace for longer exposure times. Similarly, cyclic thermal exposures will be given to these eutectics for approximately 200 hours.

E). Microscopic Analysis

The specimens will be sectioned parallel and normal to lamellar direction. A detailed microscopic analysis will be conducted using optical, scanning and transmission electron microscopy to elucidate the thermal stability of constituent phases.

3. OXIDATION AND HOT CORROSION STUDIES OF DUPONT LANXIDE ENHANCED SiC/SiC AND HITCO SiC/C COMPOSITES

A hot corrosion and oxidation study of SiC/SiC[a] and SiC/C[b] composites was conducted to examine environmentally induced interactions with the fiber and matrix and to assess the composite degradation in the simulated molten salt environment of a naval aircraft gas turbine engine. High temperature testing included both static and cyclic thermal exposures to 900°C in air for time intervals from 1 to 1000 hours. Composites were tested both as received and coated with a layer (0.5-1.0 mg/cc) of sodium sulfate. Microstructural analysis was used to examine the degradation of the composites and phase identification was performed with X-ray diffraction assisted by chemical analysis via Energy Dispersive X-ray Spectroscopy (EDS). Phase evolution and transformations were determined in-situ with the aid of a high temperature x-ray diffractometer. Degradation of these composites, being investigated for navy propulsion applications, are compared with candidate materials from previous studies (12, 13).

During combustion in a gas turbine engine, fuel contaminants such as S are converted to oxides (e.g. Na_2O, SO_2, SO_3, V_2O_5, etc.) which corrode metals and ceramics by acid-base reactions with the ceramic oxides or the protective oxide film formed on the metal or ceramic surface (e.g., SiO_2 surface layer which forms on SiC at elevated temps). The main corrodent of concern in the navy gas turbine engine environment is sodium sulfate which forms when sodium chloride (from the marine environment) and sulfur byproducts (from fuel combustion) react according to the following reaction:

$2 NaCl(v) + SO_3(g) + H_2O(g) = Na_2SO_4(l) + 2HCl$
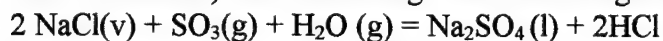
At elevated temperatures, silicon carbide oxidizes to form a naturally passivating silica layer:

$SiC(s) + 1.5O_2(g) = SiO_2(s) + CO(g)$
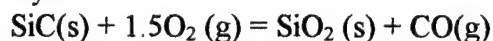
A corrosive attack of the oxidation-protecting silica layer occurs at temperatures between the sodium sulfate dew point (884C) and the vaporization point which can vary from 900-1100 C depending upon the pressures and impurity levels involved. This attack involves the formation of molten sodium silicates which permit rapid oxygen diffusion in its liquid state. Figure 4, is a micrograph of a surface of a composite which was exposed to this harsh environment. Note that the surface of the specimen was severely attacked. A thick

glassy layer (silicate) formed on the surface and easily cracked. This silicate was formed by the following reaction:

$xSiO_2(s) + Na_2SO_4(l) = Na_2O\_x(SiO_2)(l) + SO_3(g)$
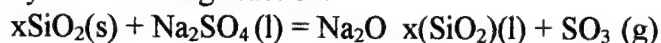
Upon cooling, e.g. as in thermal cycling during thrust-idle altering modes of operation, thermal expansion mismatches generate cracking of the glassy surface layers thereby directly exposing the SiC material to further oxidation (and the process repeats). This work has been presented elsewhere in greater detail (12, 13).

HITCO's SiC fiber reinforced C material (CERCARB^{TM}) has been specified as bill of materials (BOM) for the GE 414 engine exhaust nozzle divergent flaps and seals. The GE 414 engine is the powerplant for the new Navy F-18 E/F aircraft which runs hotter than any current jet aircraft. The attributes of the HITCO SiC/C system include; its high emissivity and thermal conductivity thereby resulting in smaller thermal gradients across the part thickness, and its oxidation protective glass-like coating (that forms at elevated temperature) and B_4C matrix particles. (This SiC/C composite system survived over 3000 engine cycles at temperatures 200-260 C higher than the superalloy nozzles in GE 414 engine tests).

The Ceramics group at NAWC has identified a spallation problem with the Hitco material on the 414. After exposure to an engine environment, the oxidation protection topcoat spalls off. Figure 5 is a micrograph of a flap that has spallation. Note the dark areas on the surface. Work is being pursued in determining the spallation mechanisms, possible solutions and/or repair options e.g. high temp corrosion resistant coatings. This involves investigating new coatings and modifiers in the coating. The goal is to increase the life of the component.

4. ALUMINIDE COATINGS FOR NAVY AIRCRAFT TURBINE APPLICATIONS

High temperature aluminide coatings are presently applied to turbine blades and vanes on most Navy gas turbine air vehicle engines. These coatings provide environmental protection for the superalloys that constitute the blade substrates. Environmental protection is provided through the formation of an adherent aluminum oxide surface layer. Although they are intrinsically protective, aluminide coatings will degrade and spall over time from a combination of oxidation, hot corrosion, and thermomechanical stresses caused by engine temperature cycling.

Components with degraded coatings must be recoated. There are a number of different methods for the reapplication of coatings, including pack cementation, physical vapor deposition, and electrophorytic deposition, and each engine manufacturer has its own set of preferred variations on these processes. It is presently specified that reapplication of coatings be done by the specific technique used in the original manufacture of the blade. The consequence of this is to limit the amount of recoating that can be performed at a Naval Depot rework facility, simply because no single facility can support such a wide range of original manufacturer processes. Even if the recoating is to be done on contract, requirement of a blade-specific coating process limits the choice of vendors.

Application of aluminide coating can be done by a number of techniques, including pack cementation, electrophorytic deposition, and physical vapor deposition. The first step in all of these processes is the deposition of a layer of aluminum to the surface nickel superalloy surface. Once an aluminum coating is applied, furnace heat treatment converts the surface to nickel aluminide through diffusion. The only difference between the various methods is in the manner of applying the initial aluminum layer. In pack cementation, samples are buried in a powder pack consisting of aluminum, a halide salt activator, and an inert filler material. Deposition of aluminum at furnace temperature takes place by chemical vapor infiltration to the sample surface. After removal from the pack, the sample is further heated to form the aluminide. In electrophorytic deposition the sample is immersed in a liquid in which aluminum particles are suspended; an electric field drives the deposition. Physical vapor deposition uses sputtered ions in vacuum to build up the initial coating.

The objective of this program is to investigate the oxidation and hot corrosion characteristics of several high-temperature aluminide coatings applied by different methods on superalloys, in order to see if the application process is truly a significant factor in the environmental resistance of coatings. A uniform set of experimental conditions (substrate alloy, specimen configuration, furnace cycle) will allow comparisons between the different coating techniques. If coating durability is found to be not a function of application technique, recommendations will be made for the Navy to simplify the system it uses to get engine turbine parts recoated. The ultimate goal of this program is to develop standard recoating processes for many different varieties of blades, which would lead to significant cost savings to the Navy.

This program employs cyclic oxidation testing, cyclic hot corrosion testing, and microanalysis including optical microscopy, scanning electron microscopy and energy dispersive spectroscopy. Coupons of three common blade alloys (IN 713, IN 100, René 80) have been coated with six different aluminide coatings: (1) Rolls-Royce RPS 320, (2) Allison Alpak, (3) GE Codep B1, (4) Pratt&Whitney PWA 70/73, (5) Allison AEP-32, and (6) PVD Al. This series includes coatings applied by three different process types: pack cementation (coatings 1-4), electrophorytic deposition (5), and physical vapor deposition (6).

Superalloy specimens were cut to 2.5x1.2x0.3cm (Figure 6). Coatings have been applied by Nadep Cherry Point (RPS 320, AEP-32, PVD Al) and several outside vendors. Samples are held in alumina crucibles for cyclic furnace exposure. The furnaces are vertical tube atmospheric type in which the samples are inserted from the top. Sample holders hang from a wire attached to a time controlled motor that moves the sample in and out of the furnace. Cyclic oxidation testing is performed at 1200°C with a cycle of 55 minutes furnace temperature, 5 minutes ambient. Samples are removed and weighed at intervals throughout a test which lasts 150 hours. Hot corrosion specimens are coated with an aqueous solution of Na_2SO_4 and air dried before being placed in the furnace crucibles. Test conditions for hot corrosion are a furnace temperature of 900°C, with cycle time and experiment time being the same as for oxidation. Specimens are washed to

remove salt coating before weighing, and the coating is reapplied before continuation of the experiment.

Three specimens for each set of experimental conditions (alloy, coating, exposure type) will be furnace exposed. Tested specimens will be cross sectioned and examined with a scanning electron microscope (SEM) (Figure 7). The surface layers - nickel aluminide and alumina - are then imaged with SEM and energy dispersive X-ray spectrometry (EDS). Interfacial interactions as seen with SEM and EDS will be correlated to specimen weight loss.

5. NAVY IHPTET MATERIALS PROGRAM

The materials part of the IHPTET (Integrated High Performance Turbine Engine Technology) Program, as with the overall program, is well coordinated among the three services and NASA. Materials development goals consistent with the Phase I & II engine tests have been established and are progressing toward sufficient maturity to be candidate materials for future military and commercial engines. The Phase I, II, & III program goals are progressively increased thrust to weight ratio from the current ~10/1 to an ultimate 20/1. The 20/1 goal is very challenging, requiring major improvements in both engine design and light weight high temperature materials.

The overall thrust of the materials work has been to emphasize reducing the weight of engine fan and compressor components while increasing or at least maintaining their service temperature capability. Also, High Temperature Turbine components are needed to withstand the very high temperatures required to increase both thrust and engine efficiency.

Work on advanced fan and compressor materials has concentrated on high temperature titanium alloy development. These include the scale-up of an orthorhombic titanium aluminide alloy, development of a gamma Ti-aluminide alloy with higher temperature capability, the development of joining techniques for these advanced titanium alloys and the evaluation of the environmental resistance of these alloys.

Combustor materials must withstand the ~2204 C flame temperature required for increased thrust and efficiency. The Navy program is qualifying a rolled sheet form of an advanced mechanically alloyed nickel alloy, MA754 for use as a combustor liner for PhaseII & III engine tests.

Hot gas from the combustor pass into the turbine whose components are among the most highly stressed in an engine. One major requirement is a turbine disk material to operate at a rim temperature of 815 C. This is ~90-120 C higher than the current capability of nickel base superalloys and represents a major development challenge. Three current development programs focus on this challenge by optimization of multiple alloy additions to the best current nickel base alloys. The best of these alloys appear capable of achieving the needed service temperature.

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ADVANCED COMPOSITE PROCESSES FOR AEROSPACE APPLICATIONS

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ABSTRACT

Advanced composite processes such as Fiber Placement (FP) and Resin Transfer Molding (RTM) are being used with greater frequency in many new aircraft programs as well as in upgrades and modifications to existing aircraft. Advanced processes provide the opportunity to automate high cost operations, such as hand lay-up, and to produce parts with less variability; in addition, automated processes improve material utilization. One of the biggest advantages of advanced composite processes is the ability to fabricate large unitized structures that combine many pieces into one large structure. This unitization of parts significantly reduces the cost of the overall airframe through minimization of assembly costs, touch labor, part tracking and quality inspections.

This paper will review some current applications of advanced composite processes on Navy aircraft and review the procedures by which these advanced processes were developed and certified for application to primary and secondary aircraft structure.

KEY WORDS: Composites, Processing, Fiber Placement, Resin Transfer Molding (RTM)

1. BACKGROUND

The two most mature Advanced Composite Processes are Resin Transfer Molding (RTM) and Fiber Placement (FP); however, there are a number of other composite processing methods which are being evaluated by various organizations in an effort to develop more affordable means of fabricating aircraft structures. Some of these processes include staging, vacuum assisted RTM, induction heating, thermoforming and electron beam curing. Each of these processes has many variations and provides significant potential to reduce the cost of airframe components. Each process is at a different state of maturity and, depending on the specific application, will have different criteria for risk assessment and acceptance. This paper will focus on the procedure used by the Navy to certify materials and processes and review some of the features and benefits of two advanced processes, RTM and FP.

Advanced processes can provide the opportunity to combine a number of parts into a larger assembly. Having one large assembly instead of many smaller parts reduces the paperwork

associated with individual parts, the quality control and inspection requirements for individual parts, the assembly steps required for individual parts and the weight associated with fasteners used to assemble many small parts into a large structure. The savings in assembly come from not only the fewer parts that must be fit into a jig but also the reduced requirement for shimming and fitting one part to the next. In addition, advanced processes can produce parts with more reproducible details such as ply drops, cut outs and build ups. In the case of RTM, high quality surfaces with precise dimensions are possible as a result of matched metal tooling used for molding.

2. PROCESS CERTIFICATION

The procedure by which the Navy develops and qualifies advanced composite processes is based on a building block approach. The process has several steps starting with simple coupons and culminating with flight test of an aircraft or component. The steps in a typical building block program include material/process selection, process development, material property development, element and sub-component testing, component fabrication and test, full scale test and flight test. The full building block program involves thousands of tests, millions of dollars and several years to complete. In many cases the procedure is tailored to the individual process which in some cases minimizes the number of specimens and amount of testing required. The building block procedure is rigorous, evaluating all aspects of materials and processes. At its completion the risk of using a process in a production environment for Navy aircraft is minimal.

Once a process is selected, the first step is to evaluate the limits of processing. For a process such as FP this involves fabricating laminates to assess variables such as material feed rates, head pressures, minimum radius and other factors related to the lay down of materials. For RTM this step would include evaluation of mold temperatures, injection temperatures and injection pressures as well as other process variables.

The next step is to develop material properties. This includes physical, chemical and mechanical properties of the material. In addition the effects of environment, defects and fatigue are determined, and appropriate knock down factors are developed. For advanced processes such as FP this would include determining if there is equivalence between hand lay-up and FP mechanical properties. This would be done in order to minimize repeating allowables testing since the material and cure process are the same as for hand lay-up. The effects of laps and gaps in the material coverage would be evaluated with respect to bearing and open hole performance. For RTM this step would include assessment of the effect of binder on physical properties, assessment of defects, and development of mechanical properties for design.

The third step in the building block procedure is to fabricate elements and subcomponents to characterize design details, damage tolerance, repair methods and manufacturing methods, and to validate the structural analysis methodology. For FP this would include fabrication of stiffened panels to evaluate impact damage tolerance, repair methods, and manufacturing procedures. For RTM this would include fabrication of stiffeners to assess cap bending and effects of defects. At this point in the building block method a process will be well characterized and a specific assessment of the risk for applying it to an aircraft can be made.

The final part of the building block procedure transitions from generic to aircraft specific tests. These last steps in the building block procedure are the most costly and complex, involving fabrication and testing of full scale aircraft and components, full scale static and fatigue tests on the ground and finally flight tests.

3. RESIN TRANSFER MOLDING

RTM is a process that has been available for many years and has been used in the sporting goods and industrial markets to make a wide variety of products. These parts are generally fabricated from fiberglass and epoxy or polyester resins. Parts are characterized by fiber volumes of 40% or less, good surface finish and void content of 2-5%. These parts have relatively complex contours, do not undergo significant loading, and could be easily fabricated in large numbers at a low cost.

The application of RTM to aerospace parts has resulted in significant changes to the process and more stringent requirements for the parts produced. Fiber volumes of between 55% and 65% and void contents of less than 1% are required to compete with prepreg lay-ups. Complex part geometries with ply drops and well-controlled fiber orientation are required to minimize weight and maximize load carrying capability. The processes and equipment used to fabricate parts of aerospace quality are significantly different than that used for other applications. Processes used to apply binders must be controlled and the equipment must maintain fiber orientation while the material is moving through the process. The cutting and handling of plies must be done in such a fashion as to not distort the fiber orientation and to align the plies properly. One of the main advantages of RTM is the ability to fabricate unitized structures which were previously constructed with several parts. Another advantage is the ability to generate high quality surfaces which are precisely oriented in space. In order to do this the tools used to fabricate parts must be of high quality and must fit together precisely. This requires high quality metallic tools with known coefficients of expansion that can resist loads applied during resin injection. The tools used to fabricate preforms and the process by which preforms are formed and consolidated are critical to the quality of the final part. The preform must fit precisely into the tool and allow the tool to close properly. This is necessary to obtain a part with nominal thickness and the required fiber volume fraction and surface finish. Finally, the processes of heating the preform and tool, injecting the resin, curing the part and removing the part from the tool have significant effects on the cost and reproducibility of the part. Automated processes in which there is limited touch labor are more reproducible and lower cost than operations that require significant operator input.

The Navy has had very limited use of RTM in aircraft structure. This is due to the significant costs of developing RTM parts and the desire to limit the number of resin types on various aircraft since only certain resins can be used in the RTM process. RTM has been used to fabricate parts when multiple surfaces are required to be of high quality and precisely located relative to one another. This precision is only possible with a matched metal molding process such as RTM. One example of this type of application is the F/A-18E/F wing flap seals. The seals maintain aerodynamic smoothness between the wing and trailing edge flaps as the flaps are engaged.

A secondary application of RTM is in the vertical tail ribs on the F/A-18E/F. The ribs were originally fabricated using a hand lay-up prepreg process over male molds. Due to thickness variations in the resultant cured parts, they required significant shimming and

rework during assembly. Through an extensive evaluation process, RTM was selected as an alternative process to fabricate these parts. The primary issues identified during the evaluation process were the need to demonstrate mechanical equivalency between hand lay-up and RTM, non-destructive testing (NDT) capability to detect defects unique to RTM, and the need to demonstrate part and process reproducibility/repeatability with RTM.

There were several areas of concern regarding mechanical equivalence. The possibility of binder migration and the effects it might have on mechanical properties was an issue. Several different 977-3 based binder systems were evaluated for ease of manufacturing. Material with the chosen binder system had to have acceptable handling characteristics and demonstrate the ability to produce highly contoured parts. Mechanical tests were performed to show that composite material produced by RTM, with the chosen binder system, had equivalent properties to hand lay-up material. Another area of concern was the determination of an acceptable processing window for RTM. Several design of experiments (DOE) studies were performed where parameters in the areas of resin preparation, tool preparation, injection, and cure were varied when producing panels to determine a process window that would prevent any reductions in properties due to the process. First, a screening DOE was performed to determine the parameters that had the greatest effect on mechanical properties. These parameters were then more closely investigated in a primary DOE to determine a process window. Lastly, to demonstrate mechanical equivalence, the fiber volume and resin content between RTM and prepreg had to be shown to be equivalent.

The second primary issue dealt with the lack of non-destructive test methods for RTM. Dissections were performed on a variety of RTM parts to establish typical RTM defects. From the photomicrographs, it was determined that resin richness and fiber waviness were the defects of concern with RTM. Approximately 20 laminates were produced containing typical defects of resin richness and fiber waviness. The capability to detect these defects was assessed for a variety of NDT techniques. An injection parameter DOE was also performed to ensure fiber wash did not occur due to the injection parameters chosen.

To demonstrate that RTM is a reproducible/repeatable process, five vertical ribs were fabricated. All the ribs passed the engineering requirements, and the destruct results compared favorably with those obtained with identical prepreg parts.

Several other issues needed to be addressed before RTM could be approved to fabricate the ribs. It was necessary to provide documentation that RTM is past the developmental stage and is ready to be implemented in production. It needed to be demonstrated that key characteristics of the RTM process are well controlled, Finally, it was necessary to show that producing these parts by RTM is more cost effective compared to hand lay-up or other advanced composite processing technologies.

Increased use of RTM in Navy aircraft will require significant work in the correlation of coupon properties with those of the actual part, the development of cost effective tooling and processing methods, and the development of a data base of mechanical properties that compares to the existing data bases for prepreg materials.

4. FIBER PLACEMENT

Fiber Placement is a process that was developed as a derivation of filament winding. FP allows for prepreg tows or slit tape to be placed at any orientation from 0 to 90 degrees on a part of complex contour. Individual bands of pre-impregnated fibers can be laid side by side over a surface. The tension, feed rate and length of an individual band can be controlled. This allows convex and concave surfaces of rapidly changing geometry to be completely covered by material. The fiber placement process is well suited for fabrication of complex shapes such as inlet ducts, fuselage skins and sponsons. In addition, the FP process has been used to fabricate large flat skins for wings and horizontal tails. FP allows for the incorporation of laid-up details such as ply drops, steps and cutouts to maximize structural efficiency. The process also has very low material scrap rate with "buy-to-fly" ratios of 1.1 to 1.2 as compared to 1.7 to 2.5 for hand lay-up.

FP has been used to fabricate several types of parts for Navy and Marine aircraft. F/A-18E/F inlet ducts, horizontal tail skins and fuselage skins have all been fabricated using FP. V-22 aft fuselage, sponsons and rotor system components have also been fabricated using FP. These parts range from very thin skins over honeycomb to thick sections of revolution.

A large building block program was used to qualify the FP process and to develop confidence in the individual companies to fabricate primary structure. The first part of the program was set up to show structural equivalency to hand laid-up prepreg material. This program developed a coupon and element test data base to show the effects of FP variables, such as laps and gaps, head speed, and pressure on mechanical properties. Sub-elements such as three stringer panels were fabricated to show shear and impact performance. Finally, demonstration inlet ducts were fabricated to show the effects of fuel pressures and hammershock on FP and hand lay-up structures. The FP ducts showed equivalency in all cases and were selected for use in production. Another FP application, the horizontal tail skin, showed similar performance to the hand laid-up version, and as a result of higher material utilization factors and lower costs, was selected for production. The success of these two parts in the F/A-18E/F Engineering and Manufacturing Development program has resulted in a decision to look at other parts that could be fiberplaced in the production program.

Based on the success of this effort and some previous work sponsored by the Air Force, the V-22 selected FP for the fabrication of the aft fuselage, the sponsons and the grip. The aft fuselage is the largest, one-piece, fiberplaced structure on naval aircraft today. It is fabricated by first placing the internal stiffeners in the tool, then fiber placing the skin over the stiffeners, and finally cocuring the whole assembly. This results in significant cost savings over separate bonding operations. The sponsons are complex honeycomb structures fabricated as one piece, consisting of inner and outer skins that are fiberplaced over a honeycomb core. This assembly is also cocured saving significant assembly steps. The last V-22 part to be fiber placed is the grip. This is a complex part that transfers load from the blades to the rotor yoke. The part is rectangular at one end and round at the other with thickness ranging from 0.5 to 3.5 inches. FP is used to place fibers along the length of the grip and to follow the complex curvature without the need for darts to eliminate wrinkles. Through the use of FP materials, costs have been reduced 38% and the manhours required to fabricate a shipset have been reduced from 2460 for the Full Scale Development grips to 978 for the production grip. FP has also allowed for a more unitized structure in which part count has been reduced from 1500 to 30(1).

While the FP process provides significant cost savings, increased material utilization and reduced part count with respect to hand lay-up, there is still a need for development of modifications to the FP process to make it more efficient and to have wider application. Modifications such as tow steering will allow more tailored structures to be fabricated. A second modification is in situ consolidation and curing for fabrication of thermoplastic and thermoset parts outside of the autoclave. In situ processing has potential to further reduce costs by eliminating the autoclave cure cycle and associated tooling. In addition an in situ process would allow the fabrication of much larger structures.

5. SUMMARY

Many advanced processes are being considered for application to aircraft structure to improve affordability and performance. The procedure that is required to evaluate new processes and provide data to address the many potential areas of risk has been described and examples of its application provided. Fiber placement is the most mature of the advanced processes and has shown significant savings compared to hand lay-up. The building block program for FP has taken several years to complete. RTM is not as mature as FP but is well along in the evaluation process. The testing and evaluation requirements for RTM are more extensive due to the fact that the resin systems in many cases are different from those used in hand lay-up and the cure conditions are significantly different from those used in an autoclave process. Other advanced processes are just starting the certification process and will require significant efforts to mature them to the point of application for primary aircraft structure.

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DIAMOND AND SAPPHIRE FOR INFRARED WINDOWS AND DOMES

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ABSTRACT

Chemical-vapor-deposited diamond is being developed as a durable bulk window material and as a coating material. Clear windows up to 1 mm thick and 60 mm diameter have been produced. Domes up to 1.5 mm thick and 75 mm in diameter have been grown and polishing is in progress. Methods have been demonstrated for attaching diamond coatings to optical windows. At 10.6 μm wavelength, the absorption coefficient is as low as 0.1 to 0.3 cm^{-1}, optical scatter is below 1%, and emissivity at 500°C is below 3%. Microwave dielectric properties, thermal properties, and most mechanical properties (except strength) of chemical-vapor-deposited diamond are equivalent to those of Type IIa natural diamond. Sapphire is the most durable, commercial window material. It has marginal thermal shock resistance for the most demanding missions because its strength falls rapidly at elevated temperature. A study of sapphire led to the serendipitous discovery that its strength above 400°C is limited by weakness in compression, not tension. Compression on the c-axis of the crystal produces twins on rhombohedral crystal planes. When twins intersect, fractures form and mechanical failure results. Understanding the failure mechanism makes possible a research program to try to improve high-temperature strength.

KEY WORDS: Diamond, Sapphire, Infrared Window

1. REQUIREMENTS FOR INFRARED WINDOW MATERIALS

Infrared sensors in military systems play a key role in target detection and weapons guidance. Delicate infrared sensors are hermetically sealed and must be protected from heat and high speed collisions with raindrops, sand, and even bugs in the atmosphere. Protection is provided by a window or dome through which the sensor sees the outside world (1). Desirable window characteristics include: (a) transparency at the desired wavelength, (b) low optical scatter, and (c) resistance to impact damage by rain and sand. For high-speed missiles, the window or dome must also have (d) low radiant emittance at elevated temperature, (e) resistance to mechanical failure by thermal shock during rapid aerodynamic heating, and (f) thermal stability. In general, materials with the best optical properties, such as alkali halides and zinc selenide, have inferior mechanical and thermal properties. There is a continual tradeoff in developing new materials with superior mechanical and thermal properties and acceptable optical properties.

TABLE 1. COMPARISON OF PROPERTIES OF INFRARED MATERIALS

PROPERTY	ZINC SULFIDE	SAPPHIRE	CHEMICAL VAPOR DEPOSITED DIAMOND
TRANSMISSION:			
Ultraviolet	No	✔	✔
Visible	Some	✔	✔
Midwave infrared	✔	✔	Thin layer only
Long wave infrared	✔	No	✔
Microwave	Poor	Poor	✔
HARDNESS (kg/mm^2)	250	2200	9000
STRENGTH (MPa)	100	700	200
THERMAL EXPANSION (ppm/K)	7	6	1
THERMAL CONDUCTIVITY (W/m·K)	19	46	2300
RELATIVE THERMAL SHOCK FIGURE OF MERIT AT 300 K	3	12	380
DIELECTRIC CONSTANT* (@ 35 GHz)	8.35	9.39 (E ⊥ c) 11.58 (E ∥ c)	5.61
LOSS TANGENT* (@ 35 GHz)	0.0024	0.00005 (E ⊥ c) 0.00006 (E ∥ c)	0.0006

*E ⊥ c and E ∥ c refers to the electric field perpendicular or parallel to the c-axis of the crystal.

Sensor systems must operate at wavelengths where the atmosphere is relatively transparent. Two transmission windows are at wavelengths of 3 to 5 µm (the "midwave" region) and 8 to 14 µm (the "long wave" region). Sapphire is the most mechanically and thermally durable of commercially available window materials. It operates in the midwave, but not in the long wave region. Diamond is under development as an extremely durable long wave window material.

When a window or dome is heated by rapid acceleration in the atmosphere, the leading surface heats up faster than the trailing surface. The hotter surface expands more than the cooler surface. In a brittle ceramic, the stress created by differential thermal expansion can be great enough to shatter the material. This is called thermal shock. A figure of merit for resistance to thermal shock is

$$\text{Thermal shock figure of merit} = R' = \frac{S\,(1-\nu)\,k}{\alpha\,E} \qquad [1]$$

where S is the strength, ν is Poisson's ratio, k is thermal conductivity, α is the thermal expansion coefficient, and E is Young's modulus. Resistance to thermal shock is favored by high strength, high thermal conductivity, low expansion, and low modulus. The greater the figure of merit, the greater the heat flux that can be withstood without shattering.

Table 1 compares physical properties of sapphire and diamond to those of a widely used long wave infrared material, zinc sulfide. Sapphire is 10 times harder than zinc sulfide, which provides sapphire with exceptional abrasion resistance. Diamond is the hardest material known and has extreme abrasion resistance (2,3). Perhaps the most remarkable physical property of diamond is its thermal conductivity, which is the highest for any material (even copper) at room temperature. Coupled with low thermal expansion, its high conductivity gives diamond an order of magnitude greater resistance to thermal shock than other infrared window materials. Another potentially useful property of diamond is that it is a good microwave window. Of the common infrared materials, only magnesium fluoride and calcium fluoride are as good as diamond for microwave transmission. Other infrared materials have high dielectric constants, which make them more reflective and therefore poorer microwave apertures.

2. DIAMOND COATINGS, WINDOWS, AND DOMES

The discovery of chemical vapor deposition (CVD) as a method for making diamond was the technological breakthrough that enabled diamond to be considered as an optical material (4). In chemical vapor deposition, a carbon source such as methane is fed into a low-pressure ($<10^5$ Pa), hot gas containing a high concentration of hydrogen atoms. Hydrogen atoms are created from H_2 by a hot filament, a microwave plasma, an electric arc, or a combustion torch. In the presence of H atoms, polycrystalline diamond is deposited from the gas phase onto a suitable substrate such as molybdenum or silicon at a temperature near 1000°C. CVD diamond can be deposited over large areas in useful shapes. By contrast natural diamond or diamond synthesized by high-temperature, high-pressure techniques can only be obtained as small crystals. Although CVD diamond can be grown with low optical quality at rates as high as tens of microns per hour, good optical quality material generally cannot be grown faster than 5 μm/h.

Bulk diamond windows are required for high thermal shock environments and highly erosive environments in which other materials would fail. However, for many applications, a thin, diamond coating can protect an underlying, softer window material.

2.1 Diamond Coatings Four different methods for attaching a thin diamond film to an optical window are shown in Figure 1. Direct growth of diamond (Figure 1a) onto most optical materials is difficult either because the material is attacked by the growth plasma or because of the large difference in thermal expansion between diamond and most other materials.
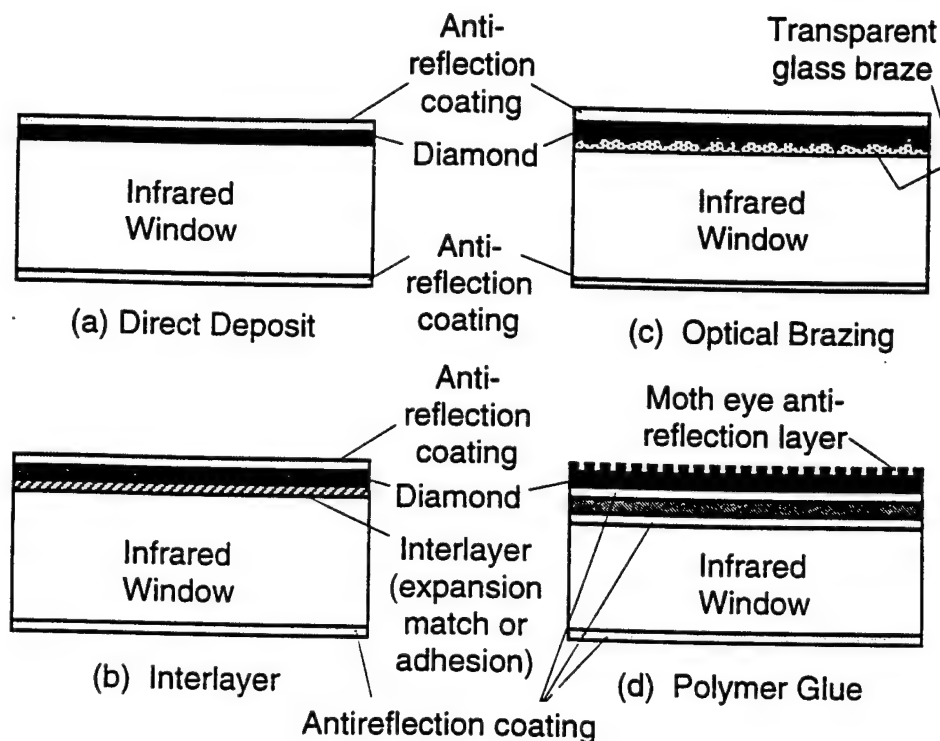
Figure 1. Methods for attaching a diamond film to an optical window.

Thin diamond coatings have been grown directly onto fused silica, sapphire and a SiO_2-Al_2O_3-ZnO glass ceramic as in Figure 1a using metal-induced nucleation of diamond (MIND) (5). In this process, a source of metal is placed in contact with the plasma near the substrate surface on which diamond is to be grown. (The diamond does not grow on the source of metal.) The source can be (a) a thin film of Cr, CrN, Ti, TiN, or Ni; (b) a metal ring containing Cr; or (c) tris(1,1,1-trifluoropentandionato)chromium(III) dissolved in acetone serving as the carbon source for diamond growth. MIND improves the nucleation and adherence of diamond and gives a growth rate of 0.4 μm/h at 650°C. Thick layers cannot be produced because thermal expansion mismatch causes delamination when the diamond thickness exceeds 5 μm.

Alternatively, a sputtered refractory interlayer (SPRINT) such as silica, hafnia, silicon carbide and aluminum nitride can be deposited onto the substrate surface as in Figure 1b and diamond can be grown directly on the interlayer (5,6). The interlayer improves adhesion and may provide a thermal expansion match. The interlayer also encapsulates the substrate to protect it from attack by the plasma and creates a diffusion barrier between the diamond and the substrate.

Instead of depositing diamond directly on a window or an interlayer, diamond can be grown separately and then bonded to the window. In optical brazing (Figure 1c), the bonding agent is a low-melting, infrared-transparent glass (7). If a glass made of As, Se, and S is used, the index of refraction of the glass is similar enough to that of the diamond that the rough surface of the diamond does not need to be polished to reduce optical scatter. However, the rough points on the diamond surface act as microindentors during raindrop impact. The coated window is more durable if the diamond is polished prior to bonding. The glass softens near 200°C.

In Figure 1d, a polymer that is transparent in the 8-12 μm long wave infrared region (but not in the 3-5 μm midwave region) serves as the bonding layer. Because the index of refraction of the polymer is not matched to that of diamond, antireflection coatings are required at every interface in this structure. The polymer softens near 150°C. Figure 1d shows a motheye coating as the outermost layer (8). This all-diamond, patterned surface provides optical impedance matching between diamond and air to reduce reflection.

2.2 Bulk Diamond Optical quality diamond (Figure 2) has been grown in disks up to 125 mm diameter and hemispheric domes up to 75 mm diameter. Thicknesses up to 2 mm have been produced, but any thickness above 0.5 mm is unusual at present.

Figure 2. Optical quality diamond window grown by chemical vapor deposition at Raytheon.

Because diamond is the hardest known material, it is extremely difficult to polish. The disk in Figure 2 was polished with abrasive diamond grit, which is very inefficient. Other polishing methods include rotation against a hot iron or nickel wheel (called a scaife) under vacuum or hydrogen (9,10), static contact with iron, cerium, lanthanum, or La-Ni eutectic at 600-900°C under Ar (11-13), use of ion beams (14,15) and laser ablation (16). The difficulty with any of these methods is controlling the optical figure (the exact required geometry) of the workpiece.

Fig. 3 shows an as-grown, non-optical-quality CVD diamond dome with a very rough outer surface and a partially polished dome. The outer surface of the as-grown dome was first machined with a laser to reduce the roughness by more than an order of magnitude to <5 μm. Final polishing with abrasive diamond grit removed graphite produced by the laser and further reduced the surface roughness. Polishing diamond with diamond abrasive is so inefficient that it was not possible to achieve an optical finish with this particular dome. To produce a better optical finish, it appears necessary to achieve a shape and roughness much closer to the final requirement in the step prior to abrasive polishing.

3. PROPERTIES OF CVD DIAMOND

Table 2 summarizes properties that have been achieved for CVD diamond and compares them to properties of Type IIa diamond (17,18). Figure 4 shows the infrared transmittance of a 1.25-mm-thick diamond window before and after receiving an antireflection coating on both sides.
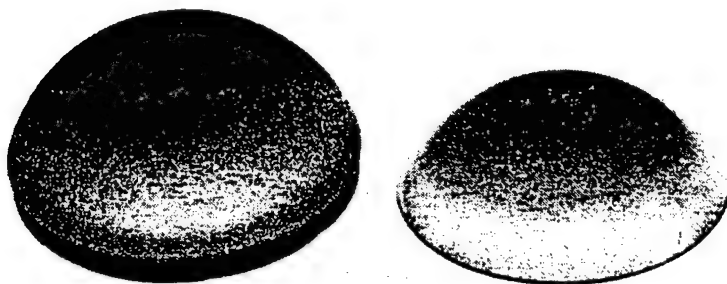
Figure 3. Raytheon as-grown, non-optical quality, CVD diamond dome (*left*) with surface roughness of ~50-100 μm. Laser machining and abrasive polishing produced the smooth dome (*right*) with an outer radius of 35 mm and a thickness of 1.5 mm.

The theoretical maximum transmittance of diamond near 10 μm wavelength, where absorption is low, is 71.4% because diamond reflects 28.6% of incident radiation at this wavelength. The litmus test for "optical-quality" diamond is the transmittance of a thick (>0.3 mm), polished specimen. Good optical-quality material has close to the theoretical transmittance in the long wave (8-14 μm) region, but has significant absorption in the midwave (3-5 μm) region. At high temperature, materials emit radiation at wavelengths where they absorb radiation. Therefore, even high quality diamond emits significant radiation in the 3-6 μm region when the window is heated. CVD diamond with more than a few ppm of hydrogen has sharp C-H absorptions near 3.4 μm and weak, broad absorptions in the 1-phonon diamond region at 8-10 μm.
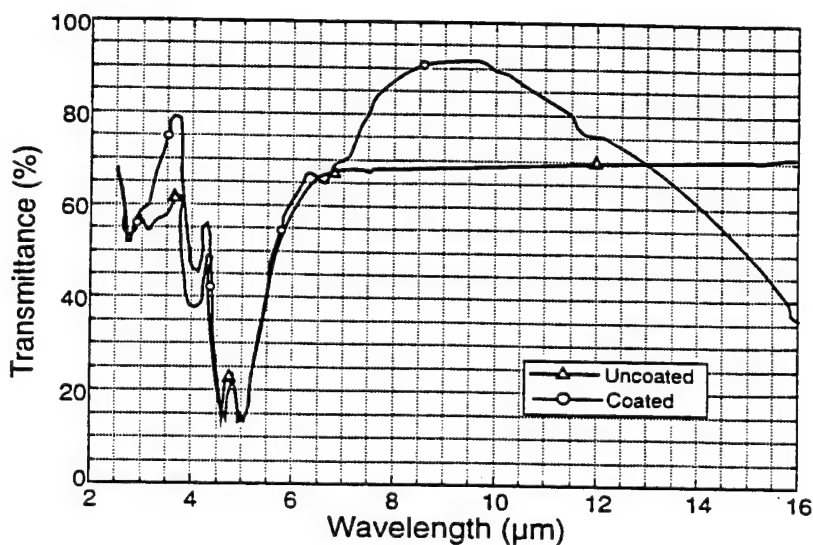
Figure 4. Infrared transmittance of diamond plate (1.25 mm thick × 64 mm diameter) before and after receiving an anti-reflection coating on both surfaces. The theoretical maximum transmission of 71.4% is limited by 28.6% reflection from a diamond plate.

The mechanical tensile strength of CVD diamond is far below the values of 2-3 GPa cited for small samples of natural, single-crystal diamond (20,21). Fig. 5 shows measurements of the flexure strength of diamond disks that were cut from 125-mm-diameter plates and tested in the as-grown condition (i.e., unpolished). The following conclusions were reached: (a) The smooth, fine-grain substrate surface of CVD diamond is significantly stronger than the rough, coarse-grain growth surface. (b) The strength of the substrate surface depends on the thickness of the diamond, but the strength of the unpolished growth surface is independent of thickness. (c) The strength of the substrate surface of very thin samples (~100 μm) is as great as 1000

TABLE 2. COMPARISON OF PROPERTIES OF CVD DIAMOND AND NATURAL (GEM-QUALITY) TYPE IIA DIAMOND

Optical absorption coefficient @ 8-12 μm wavelength

Gem (IIa) diamond: 0.03-0.05 cm^{-1} @ 10.6 μm @ 20°C

CVD diamond: 0.1 - 0.3 cm^{-1} @ 20°C
         CVD absorption coefficient @ 8-12 μm is ~2x as great at 500°C as at 20°C

Emittance @ 8-12 μm wavelength

CVD diamond: 0.02 @ 300°C (sample thicknesses = 0.35 - 0.77 mm)
                0.03 @ 500°C (sample thicknesses = 0.35 mm)

Integrated forward optical scatter

Gem (IIa) diamond: 0.2% (@ 0.63 μm integrated from 0.3 to 45°)
(0.3-0.5 mm thick)   0.004% (@ 10.6 μm integrated from 1.1 to 45°)
CVD diamond: 4% (@ 0.63 μm integrated from 2.5 to 70°)
(0.35-0.77 mm thick)   0.2-0.8% (@ 10.6 μm integrated from 2.5 to 70°)
         (There is no significant change in the range 20-500°C)

Refractive index @ 10 μm wavelength

Gem (IIa) diamond: 2.376

CVD diamond: 2.38; dn/dT = 15.6×10^{-6} K^{-1} (7-12 μm, T = 295-784 K)

Microwave dielectric properties (T = °C)

Gem (IIa) diamond: Dielectric constant (ε) = 5.61 ± 0.05; tan δ = $(6\pm3) \times 10^{-4}$

    (@ 35 GHz) $100\Delta\varepsilon/\varepsilon_{18°C} = -0.026 + 0.006886T + 3.831 \times 10^{-7}T^2 + 1.185 \times 10^{-8}T^3$
    (T = 18-525°C)

CVD diamond: Dielectric constant = 5.7; tan δ < 4×10^{-4} (@ 13.6 GHz)

Thermal conductivity

Gem (IIa) diamond: 2300 W/m·K(20°C); 1300 W/m·K (480°C); 500 W/m·K (700°C)
CVD diamond: 2000 W/m·K (20°C); 1200 W/m·K (480°C)

Thermal expansion coefficient

Gem (IIa) diamond: 1.0 ppm/K (300 K); 2.7 ppm/K (500 K); 4.4 ppm/K (1000 K)
CVD diamond: Same as natural diamond

Hardness

Gem (IIa) diamond: 76 - 115 GPa (anisotropic)
CVD diamond: 81 ± 18 GPa (decreases by 30% at 800°C)

Fracture toughness

Gem (IIa) diamond: ~3.4 MPa$\sqrt{m}$

CVD diamond: 2-8 MPa$\sqrt{m}$; 5.3 ± 1.3 MPa$\sqrt{m}$; 8 ± 2 MPa$\sqrt{m}$

Young's modulus / Poisson's ratio

Gem (IIa) diamond: 1143 GPa / 0.069 (average of anisotropic values)
CVD diamond: Consistent with gem diamond value

Mechanical strength

Gem (IIa) diamond: ~3 GPa (tensile strength)
CVD diamond: ~200 - 400 MPa (No loss of strength at 1000°C)
   (0.5-1 mm thick, polished disks tested by ring-on-ring flexure; load radius = 4.88 mm, support radius = 8.61 mm)

Water jet damage threshold velocity (19)

(0.8 mm diameter jet; 1-mm-thick, optical-quality diamond on solid backing)
   Gem (IIa) diamond: ~580 m/s jet velocity
   CVD diamond: 200-250 m/s (central crazing); 350-500 m/s (ring fracture)

MPa. Strength decreases significantly with increasing thickness in the range 100-400 μm and then levels off at ~300-450 MPa. (d) The strength of the rough, unpolished growth surface is ~150 MPa, independent of thickness. (e) Polishing the growth surface of specimens from run MP3-58 increased the strength by ~50%. (f) There was no significant difference in the strength of diamond cut from near the center or near the edge of 125 mm disks. (g) The standard
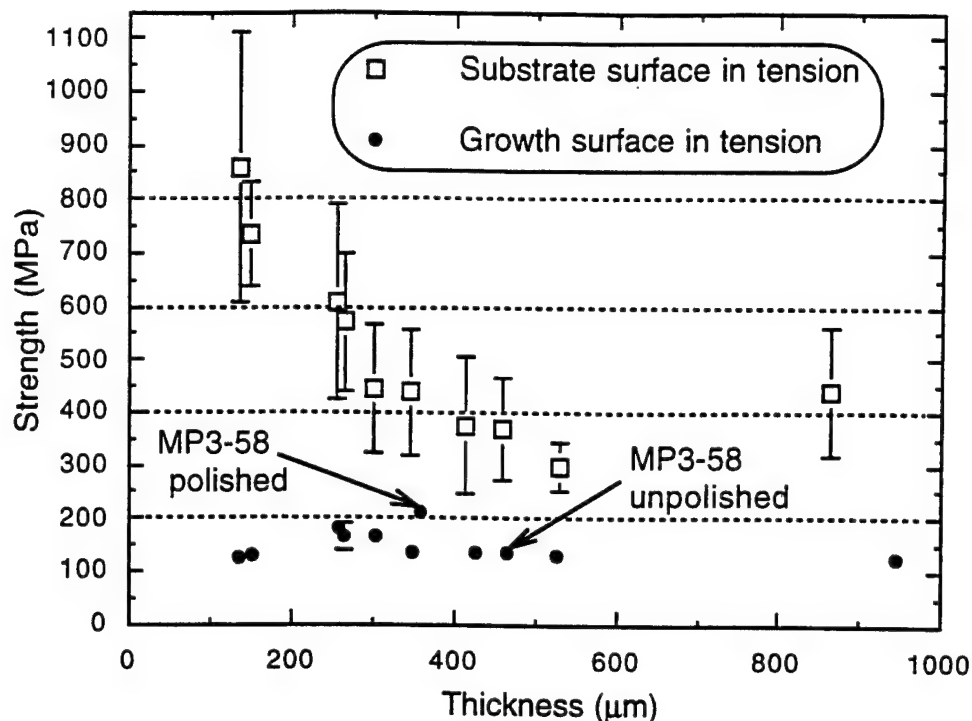
Figure 5. Dependence of mechanical strength of Raytheon CVD diamond on growth thickness. Diamond plates were cut with a laser into disks and fractured in the as-grown state (without polishing). Disks with a diameter of 17 mm were supported on a 14-mm-diameter support ring and fractured with a 7-mm-diameter load ring at a crosshead speed of 1.27 mm/min. The tensile surface is the side of the disk placed in tension during the flexure test. The smooth substrate surface of the diamond faces the substrate during diamond deposition and has a very fine grain size. The rough growth surface faces the plasma during deposition and has a coarse grain size.

deviation of strength of the growth surface is much smaller than the standard deviation of strength of the substrate surface.

For comparison to Figure 5, 3-point bending tests of 2 × 20 mm diamond bars from DeBeers with a thickness of 0.8 mm gave a strength of 460 (±40) MPa for the growth (coarse grain) surface and 990 (±55) MPa for the substrate (fine grain) surface (22). The flexure strength of 0.25-mm-thick × 6.4-mm-diameter CVD diamond disks from Norton, General Electric, and Diamonex was 230-410 MPa (23). The burst strength of DeBeers CVD diamond disks with diameters of 14 or 25 mm and thicknesses of 0.18-0.32 mm was 746-1079 MPa (24). General Electric diamond is reported to have a burst strength of 891-1162 MPa for 10-mm-diameter disks with a thickness of 0.22-0.30 mm (25). Four-point bending tests of 5 × 25 mm diamond bars from Crystallume with a thickness of 0.13 mm gave an average strength of 570 MPa (standard deviation = 120 MPa) (26). Although there may be some significant variation (perhaps a factor of 2) in the strength of optical quality CVD diamond from different sources, most of the variations in reported strength can be attributed to variations in the sample geometry and test method.

4. HIGH-TEMPERATURE STRENGTH OF SAPPHIRE

In contrast to CVD diamond, which is made up of individual microscopic crystallites, sapphire is single crystal of aluminum oxide (Al_2O_3) (27). Figure 6 shows commonly observed faces of natural sapphire crystals and identifies the directions c, a, and m, as well as the rhombohedral (r) crystal planes. The c-axis, which is the highest (3-fold) symmetry axis of the crystal, is also called the optical axis. Although the properties of sapphire in Table 1 are by no means as extreme as those of diamond, sapphire is the most durable, commercially available infrared window material. Compared to other infrared materials, sapphire has the second best erosion
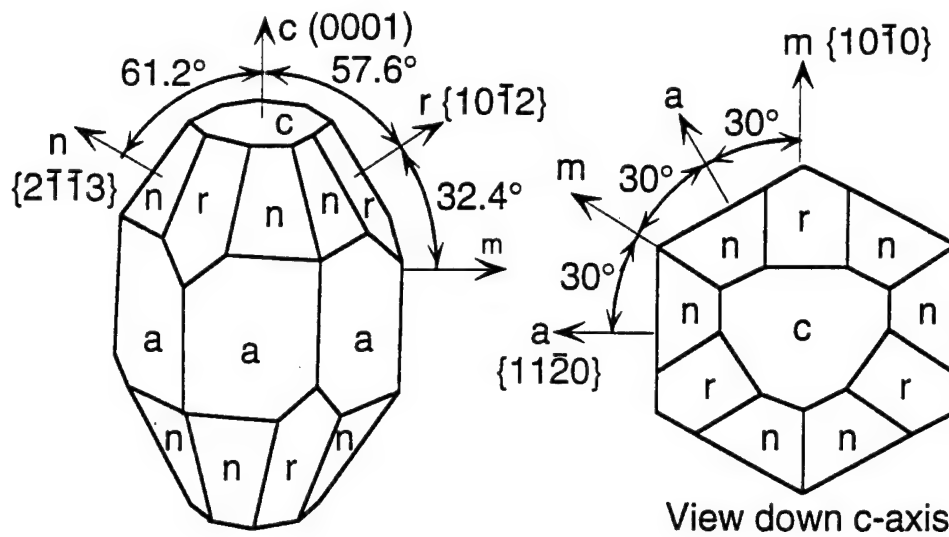
Figure 6. Sapphire crystal.

resistance (only diamond is better) and excellent thermal shock resistance. Unlike diamond, which only operates in the long wave region, sapphire is restricted to the midwave region.

Oxide ceramics generally have fairly constant mechanical strength between room temperature and 600°C. In sapphire, however, the strength decreases steadily up to 600°C in many types of specimens, and then gradually climbs again (28-36). A more detailed examination of the strength of sapphire as a function of crystal orientation unveils the two extreme behaviors in

Sapphire forms twins on the rhombohedral crystal planes (r-planes in Figure 6) when it is compressed along an appropriate axis at elevated temperature (38). The twin shown schematically in Figure 8 is a plane in which the crystal lattice is reoriented from the original lattice on either side of the twin. Twinning on the r-plane of sapphire results in a shrinkage of the crystal in the c-direction. Therefore compression, but not tension, along the c-axis causes twinning.
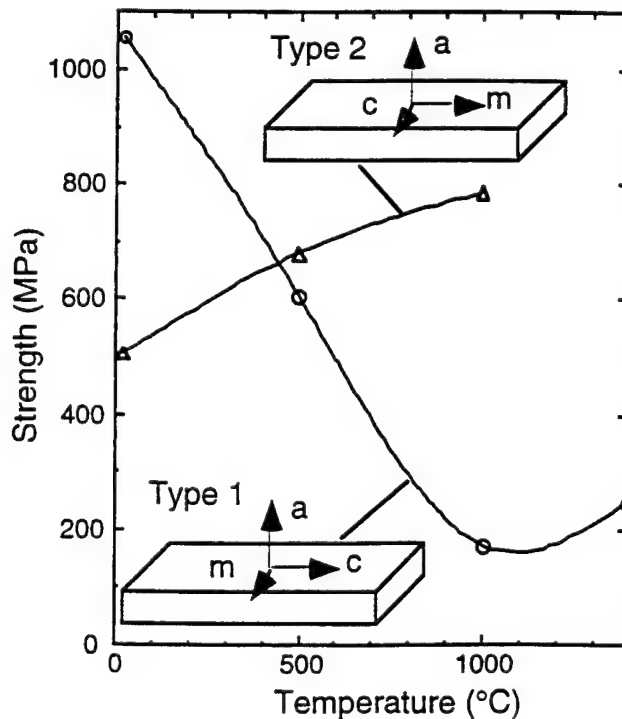
Figure 7. Strength of 3×4×45 mm optically polished sapphire bars in 4-point flexure tests.
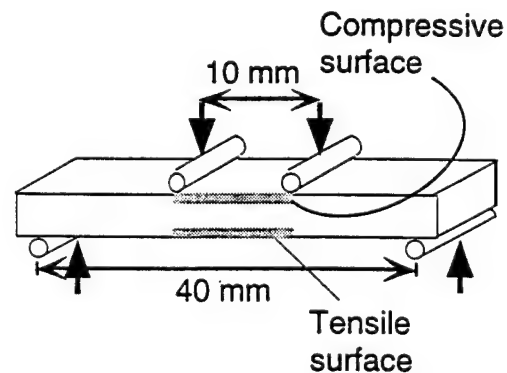
Figure 7 (37). When the c-axis of the crystal is the tensile axis of a 4-point flexure specimen, the strength drops most dramatically (Type 1 bar in Figure 7). When the c-axis is neither the tensile axis nor parallel to the loading direction, the strength actually increases with increasing temperature (Type 2 bar).

c-axis
compression

c-planes

c-axis

Rhombohedral
twin

r-plane

Shear
required
for r-plane
twinning

15.2°

32.4°

Single crystal

Twinned crystal
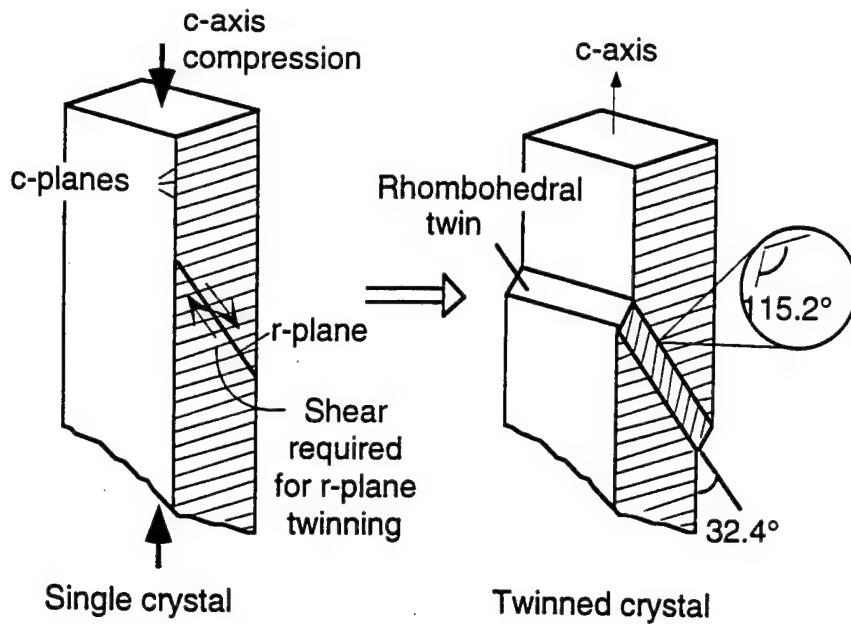
Figure 8. Formation of a twin on the r-plane of sapphire by compression on the c-axis of the crystal. Atoms in the twin shift somewhat to effectively reorient the crystal lattice within the twin.

It is possible to explain many unusual aspects of the mechanical strength of sapphire in terms of twinning induced by c-axis compression. The most extreme behavior is seen in pure compression and pure tension tests such as those in Figure 9. The c-axis and a-axis tensile strengths of sapphire do not change very much with increasing temperature between 20° and 800°C. Furthermore, the a-axis compressive strength is also fairly insensitive to temperature. However, the c-axis compressive strength falls steadily to just 3% of its room temperature value by 600°C.

The explanation for this behavior is based on r-plane twinning induced by c-axis compression. In Figure 6 there are three r-planes disposed at 120° intervals about the c-axis. If a twin forms on one of the r-planes, there is a reorientation of the atoms in the lattice within the twin. If twins form on two different r-planes, the atoms move in different directions in each twin. When twins on two different r-planes intersect, the atoms in the intersection are attempting to move in two ,
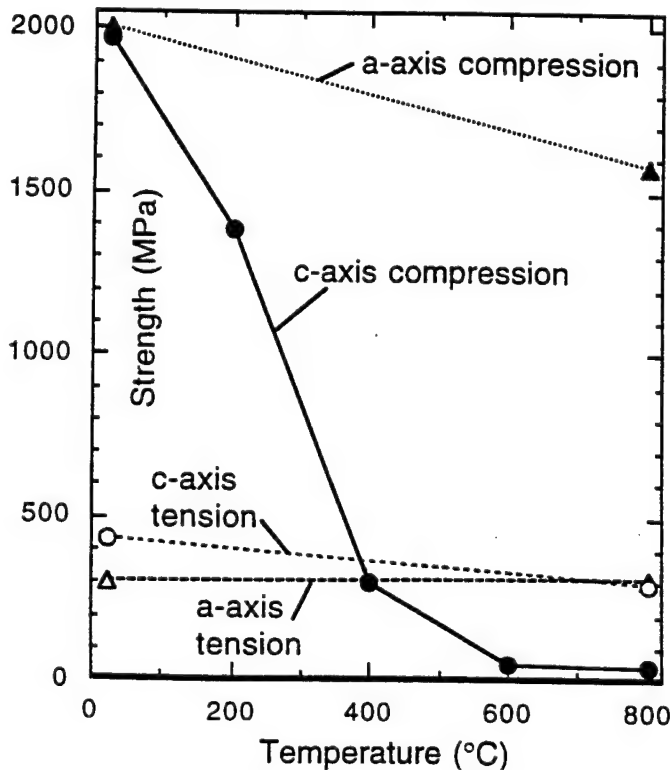
Figure 9. Temperature dependence of the strength of sapphire in pure compression and pure tension on two different crystal axes.

Compression cylinder

3.18 mm diameter
6.35 mm length

Tensile specimen

165 mm length
6.35 mm gauge diameter
35 mm gauge length

a-axis compression

c-axis compression

c-axis tension

a-axis tension

Strength (MPa)

2000

1500

1000

500

0

0   200   400   600   800

Temperature (°C)

different directions and a fracture inevitably occurs at the intersection. Once a fracture formsthen the sapphire is subject to ordinary tensile failure originating at the crack. The loss of strength in sapphire at elevated temperature is therefore attributed to c-axis compression causing intersecting twins that cause cracks to form. If tensile stress is present in the region of the crack, then mechanical failure results.

The contrasting behavior of Type 1 and Type 2 bars in Figure 7 is explained in the following manner: During a flexure test, Type 1 bars are subjected to tensile stress on the lower surface and compressive stress on the upper surface. Compression along the c-axis at elevated temperature causes twinning on the upper surface and the twins propagate to the lower surface. When twins on different r-planes intersect in the tensile field at the lower surface, fracture and failure results (37). In Type 2 bars, the c-axis is not subject to any significant tension or compression and strength is not lost up to at least $1000°C$. If the c-axis is rotated $90°$ (exchanging the a and c directions in the Type 2 bar), contact compression with the rollers in the c direction causes twinning and failure at the outer load points (36,37).

Understanding the mechanism of strength loss in sapphire enables a research program to be undertaken to try to increase the high temperature strength of sapphire. Failure occurs because of compression-induced twinning, which is thought to be a property of the perfect bulk crystal. Any disruption of the crystal lattice that retards twinning could increase the high temperature strength of sapphire by preventing twins from propagating through the crystal. This could be achieved by doping with foreign atoms, introducing crystal defects into the lattice, or even introducing small quantities of a second crystalline phase into the sapphire. Each of these approaches is presently under investigation.

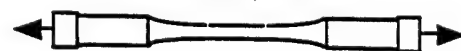Increasing the high temperature strength of sapphire translates directly into increased thermal shock resistance. Such an improvement would make this already robust material even more durable for the most demanding infrared window applications.

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6. BIOGRAPHY

Dan Harris specializes in infrared-transmitting ceramic materials at China Lake, where he has been since 1983. He earned degrees in chemistry from Massachusetts Institute of Technology (S.B., 1968) and California Institute of Technology (Ph.D., 1973). In a previous life, he taught chemistry at the University of California at Davis and at Franklin and Marshall College. He authored the book *Infrared Window and Dome Materials* (SPIE Press, 1992) and has written the leading textbook in undergraduate analytical chemistry, *Quantitative Chemical Analysis* (4th ed., W. H. Freeman, 1995), as well as two other chemistry textbooks.

OPTICAL AND ELECTRONIC MATERIALS FOR NAVAL AVIATION

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ABSTRACT

Electrooptic polymers are materials whose index of refraction change upon application of an external electric field. These materials have found use in various types of light modulators. A brief introduction to electrooptic materials will be given followed by current progress and challenges will be reviewed. The second portion of the talk will cover electrically conducting polymers, which have been the subject of intense study for about 2 decades. Conducting polymer projects at the Chemistry and Materials branch at China Lake range from synthesis of novel conducting polymers to the use of existing conducting polymers for corrosion protection and as electrochromic windows. Recent progress in the area of corrosion protection will be presented.

KEY WORDS: Electrically Conductive Polymers, Nonlinear Optical Polymers, Corrosion Protection, Electro-optic Modulators, Polymer Devices.

1.   ELECTROOPTIC POLYMERS

1.1 Introduction

Electrooptic polymers are polymers that contain units (called chromophores or dipoles) which have large hyperpolarizabilities. These chromophores have the ability to maintain a *non-centrosymmetric* charge separated state. For the most part, these chromophores contain strong electron donating groups and strong electron withdrawing groups separated by a conjugated bridge. This property is explained, albeit simplistically, in Figures 1a-b.
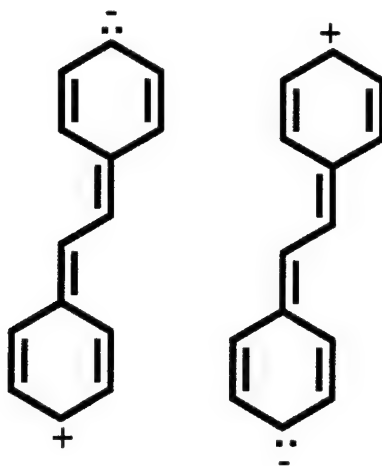
Figure 1a: Charge separated States of Stilbene

The structure shown in Figure 1a, charge separated states of stilbene, are not only extremely difficult to maintain, but also the opposing charge separated state is equal in energy, therefore, stilbene has a zero hyperpolarizability.
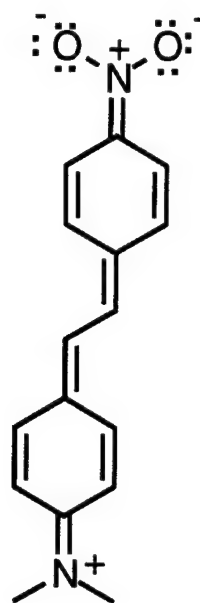
Figure 1b: Charge Separated State Of Dimethylaminonitrostilbene.

The structure in Figure 1b, the charge separated state of Dimethylaminonitrostilbene, (DANS), is much easier to maintain and the opposing charge separated state (with a negative charge on the amine nitrogen) is essentially impossible. Therefore, DANS has a large quadratic hyperpolarizability.

Not only is it necessary for the material to contain chromophores with high hyperpolarizabilities, but it is also necessary to have the chromophores aligned in a bulk non-centrosymmetric fashion (macroscopic polar order). That is, all the electron withdrawing ends of the chromophores must be pointing in the same general direction. This is usually achieved by heating the polymer above or near its glass transition temperature while a strong electric field is applied through the thickness of the film, then cooling the polymer film to room temperature with the electric field still turned on. This process is called poling[1].

It is also necessary to maintain this electrooptic coefficient for long periods of time (see section 1.3). This is done by either immobilizing the chromophore in a polymer matrix, or incorporating the chromophore into the polymer backbone. Generally, the higher the glass transition temperature the more stable the electrooptic coefficient.

1.2 Devices

Once the above listed requirements are met, the electrooptic material, when placed under an external electric field, will undergo a change in index of refraction. There are many types of devices which can exploit this phenomenon. Most notably is the Mach-Zehnder Interferometer, which uses the Pockels effect to modulate the intensity of light. In this particular device, the light path is split into two arms. Light in one arm goes through an area with electrooptic polymer (an electric field is placed across the polymer) changing the index of refraction and thereby changing the phase of the light in the arm. If the light from this arm is 180° out of phase with the light from the other arm, the two arms will destructively interfere when recombined. The nature of this modulation in electrooptic polymers makes modulation frequencies of 40 to 100 GHz possible[2].

There are several applications that can exploit this interesting technology. Photonic control of phased array radar, high speed reflection modulators[3], waveguide switches[4] and optical transmitters for connecting CMOS integrated circuits[5] are all applications that will take advantage of electrooptical polymers.

An excellent overview of nonlinear optical polymer synthesis, characterization and devices is in the literature[6].

1.3 Device Requirements

Having materials with large hyperpolarizabilities is not the only criterion that needs to be met. There are several other device requirements that these materials must meet or exceed:

- Electrooptic signal stability for 10 years at 85°C. This means that the glass transition temperature of the polymer matrix must be at least 200°C.

- Electrooptic coefficient (r_{33}) of at least 20 pm/V for reasonable device sizes (1 cm in length). Combined optical loss (absorption, reflection, scattering) in the device must be at most 3 dB (50% transmission for a 1 cm long device).

- Thermal decomposition temperature of at least 50°C above the glass transition temperature (can be defined as the temperature at which 2% weight loss is seen) when performed under nitrogen. This allows for a sufficient processing window; the polymer will remain chemically stable when heated near its glass transition temperature.

These requirements will also change slightly depending on individual applications, but they are generally used to guide the synthesis of new electrooptical polymers. To this end, the following polymer, shown in Figure 2 was synthesized.
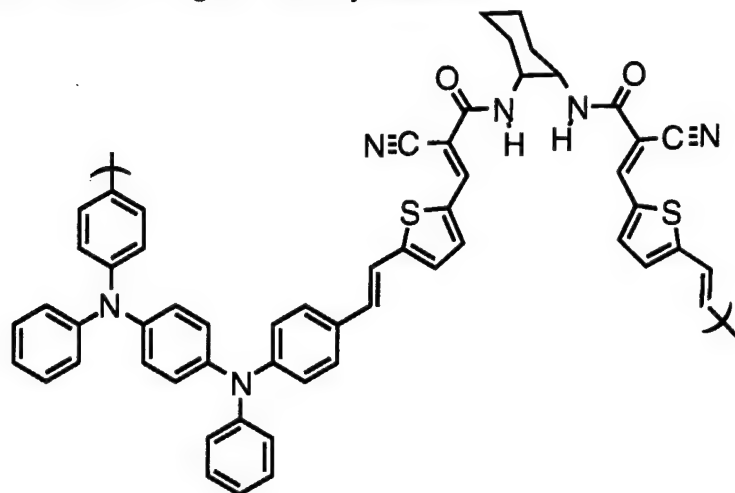
Figure 2: High Glass Transition Nonlinear Optical Polymer

This polymer has a glass transition temperature of 240°C, a decomposition temperature of 320°C, an estimated r_{33} of around 17 pm/V. The combined optical loss (measured at 1.3 μm wavelength) of this material in a 1 cm device is between 5-10 dB/cm[7], which is too high, even for an accurate r_{33} measurement. It is possible that the thermal history of the polymer may be responsible for the high loss coefficient, or that the polymer has an intrinsic absorbance. The nature of this loss is under investigation.

2. ELECTRICALLY CONDUCTING POLYMERS

2.1 Introduction

The groundwork to conducting polymers was performed back in the 1960s where Pohl, Katon and others first synthesized and characterized semiconducting polymers and conjugated polymers[11]. About 10 years later, the discovery of the high conductivity of poly(sulfurnitride) $(SN)_x$, a polymeric inorganic explosive[12] and its interesting electrical properties was a step towards conducting polymers as they are known today.

Conducting polymer research started nearly 25 years ago, after films of polyacetylene were found to exhibit profound increases in electrical conductivity (the first report of polymers with high electrical conductivity) when exposed to iodine vapor[20,21]. The procedure for

synthesizing polyacetylene was based upon a route discovered in 1974 by Shirikawa through accidental addition of 1000 times the normal amount of catalyst during the polymerization of acetylene[22].

There have been several reviews on conducting polymers. Conducting polymer research is evolving rapidly enough that yearly reviews are almost necessary. Today, there are hundreds of articles on conducting polymers research published every year.

Poly(acetylene) (PA)
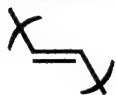
Poly(aniline) (PANI)
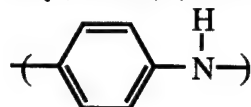
Poly(pyrrole) (PPy)
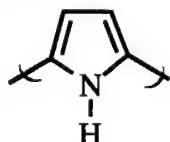
Poly(thiophene) (PT)
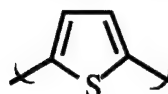
Poly(para-phenylene vinylene) (PPV)
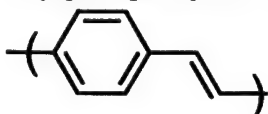
Poly(3,4-ethylenedioxythiophene) (PEDOT)
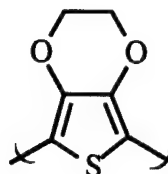
Poly(para-phenylene) (PPP)

Figure 3: Structures Of Conjugated Polymers In Their Respective Neutral Forms.

Figure 3 shows structures of some conducting polymers in their respective neutral forms. Almost without exception, all conducting polymers are the cation salts of conjugated polymers. The conjugation is necessary to stabilize the cation throughout the polymer backbone. This stabilization manifests itself in making it easier to remove an electron from the polymer backbone, which lowers the oxidation potential. Generally, the lower the oxidation potential, the more stable the conducting form of the polymer. As an example, PPy has an oxidation potential around -0.4 Volts vs. SCE and its conducting form is very stable, PPV has an oxidation potential around 0.75 Volts versus SCE and its conducting form is very unstable.

One way to influence (lower) the oxidation potential is to add electron donating groups to the polymer backbone. The groups are usually added to the monomers and then the monomers are polymerized because complete reactions on polymers are often extremely difficult. When dialkoxy groups are incorporated into the PPV backbone, the resulting dialkoxy PPV has an oxidation potential close to 0.2 Volts vs. SCE and the conducting form is stable in air. Polymers with oxidation potentials less than 0.5 Volts vs. SCE have conducting forms that are fairly stable in air.

The addition of side groups to the polymer backbone can also be used to influence the solubility of the materials, thus enabling fine tuning of properties required for processing. There are some general empirical rules which allow one to obtain reasonable estimates of polymer conductivity.

2.2 Synthesis of Bis(dialkylamino) Substituted PPV

The addition of bis(dialkyl amino) substituents on to the PPV backbone is of interest for several reasons. First the amino groups are generally stronger electron donors than alkoxy groups (provided that the resulting amino substituted polymer structure is planar) and should bring the oxidation potential of the polymer down around 0 Volts vs. SCE, making the conducting polymer even more stable. Next, amine functionalized polymer should adhere fairly well to aluminum. Finally, amino groups also can be quarternized, which could be exploited to make the polymer water soluble.

The synthesis of amino functional PPV presented some serious synthetic challenges[40]. Usually, a radical halogenated step is used in making the precursors to PPV. For example, 1,4 dimethyl benzene would be chlorinated or brominated to make a precursor to PPV. Although this method can be adapted well for the alkoxy derivatives, it can not be used for amino derivatives because the reaction is dangerously exothermic. The danger of this type reaction was established back in 1957, when a fatal accident occurred[41]. Another method, used generally for dialkoxy derivatives, is to chloromethylate the dialkoxy substituted compounds. This reaction will not work with amines because the acidic conditions used will protonate the amine making it unreactive.

Therefore, another synthetic strategy was developed. This method, shown in Figure 4, does not involve any of the above mentioned problem steps.
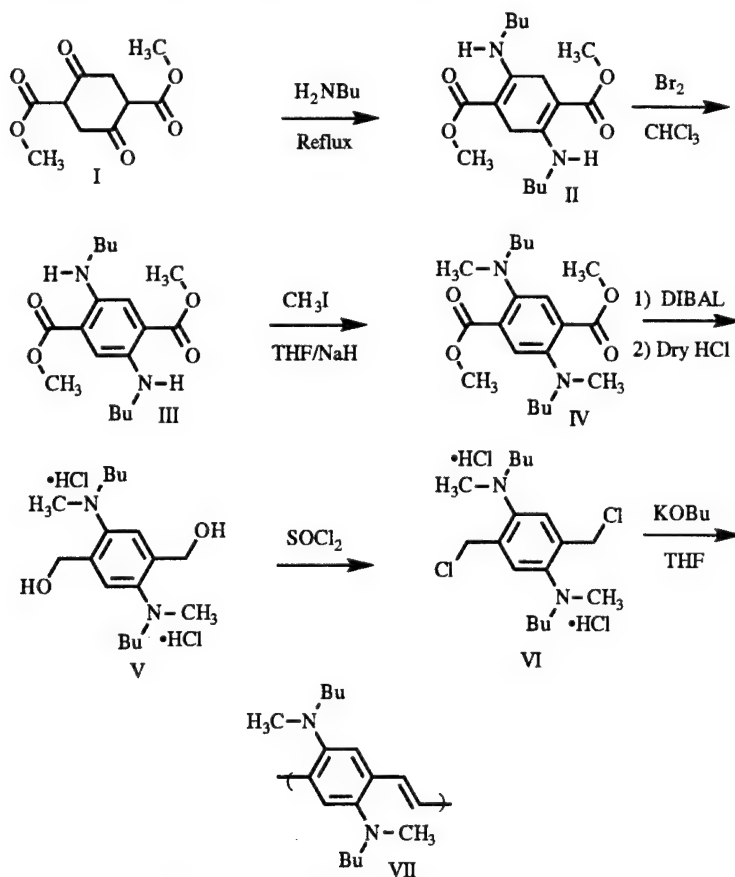
Figure 4: Synthesis of Bis(dialkylamino) PPV

This method allows the synthesis of fairly pure polymer[42] and is being improved to allow for scale up. The electrical and electrochemical properties of this polymer are currently being studied. The neutral form of the polymer is orange-red in color and the absorption maximum is 460 nm. This absorption maximum is much higher in energy than expected, so it is possible that the polymer backbone is non-planar.

2.3 Corrosion Prevention

The prevention of corrosion on aluminum[43] is a critical need for many civilian and military ships, airplanes[44], and missiles[45]. There are also many environmental concerns. One of the current methods used to inhibit corrosion involves chromium, a very toxic heavy metal. Although chromium works well against corrosion, it does get released into the environment (this is a particular problem when ships are at port). Conducting polymers have the potential to meet this need. Polyaniline (PANI) has been used as a corrosion protective coating for several substrates[46]. However, PANI has some adhesion problems with aluminum.

Adding amine substituents to PPV could result in a polymer with good adhesion to aluminum and good corrosion inhibiting properties. In fact, it was found that bis(dialkylamino) PPV films adhere very well to aluminum (see section 2.5).

2.4 Corrosion Experimental

Immersion studies were performed on aluminum T3 plates (5.1 x 5.1 x 0.15 cm), one coated with bis(dialkylamino) PPV and the other uncoated in side-by-side alternate immersion studies for 1 month. Each plate had a 4 cm scribe mark. The films were immersed in isotonic sea water at pH 8.1 for 24 hours then exposed to air for 24 hours.

Another similar immersion test involved the use of type II anodized aluminum, one coated with bis(dialkylamino) PPV, the other uncoated.

Films of bis(dialkylamino) PPV were cast on type II anodized aluminum T3 plates. The electrochemical studies were conducted in concentrated salt water solutions by dissolving approximately 70 g of sea salt into 1200 mL of deionized water. This produced a solution that was of similar pH (~8.1) and composition as sea water. Both potentiostatic and galvanostatic electrochemical studies were performed versus Ag/AgCl.

2.5 Corrosion Results

For the aluminum T3 plates, the results from the alternate immersion studies indicated significant reduction in corrosion for the polymer coated sample, even in the area with the scribe. It was difficult to find the scribe mark on the uncoated sample. The study with anodized aluminum T3 plates indicated some reduction in corrosion for the polymer coated sample. In both the coated regular aluminum and coated anodized aluminum plates, the conducting polymer film still showed excellent adhesion after the immersion tests.

Figure 5 shows the results of the potentiostatic studies on the coated and uncoated anodized aluminum plates.
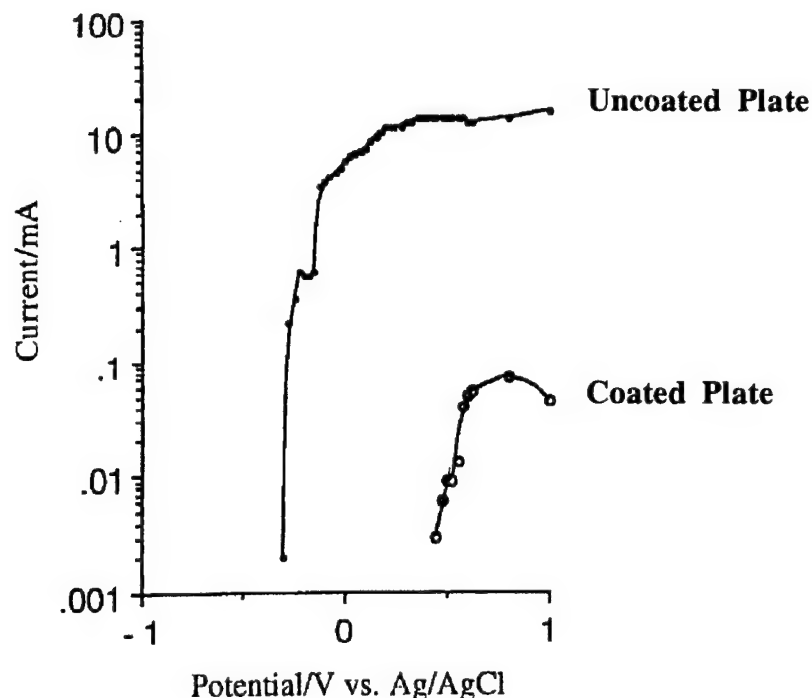
Figure 5: Electrochemical Behavior of Coated and Uncoated Anodized Aluminum T3 Plates

The electrochemical studies indicated a maximum current of 25 mA at 3.00 V vs. Ag/AgCl for the uncoated anodized T3 plate. The potentiostatic study yielded a total current of 1.380 coulombs. Close examination of the plate showed a few isolated regions on the edges of the plate to be the main contributors to the anodic current. Specifically, there was no measurable current from -0.6 to -0.3 V, with pitting potential around -0.28 Volts (untreated T3 has a pitting potential around -0.6 V). The results for the polymer coated plate indicate a pitting potential near 0.525 V. The anodic current increased only slightly to 0.071 mA at 0.8, and then *decreased*. There was no further increase in current observed out to 3.0 V. The potentiostatic study yielded a total current of 0.00358 coulombs. This is quantitative evidence that bis(dialkylamino) PPV can be used to prevent corrosion on aluminum plates.

The initial results about the corrosion inhibiting properties of amino PPV are very promising indeed. However, there are many other tests that need to be performed before amino PPV can be incorporated as a substitute for chromium.

3. SUMMARY

Both electrically conducting polymers and electrooptic polymers have the potential to make a significant impact on Naval Aviation. Ultrafast modulators and other electrooptical switches, achievable with electrooptic polymers, will allow the near real-time transmission of data. Conducting polymers also show great potential for environmentally friendly corrosion protecting coatings, and as materials for electrochromic windows.

ACKNOWLEDGMENTS

BIOGRAPHIES

John D. Stenger-Smith was born in Philadelphia, PA in 1961. He received a Bachelor of Chemical Engineering from the University of Delaware in 1984 and a Ph.D. in Chemical Engineering under the direction of Prof. Robert W. Lenz from the University of Massachusetts at Amherst. Most of the experimental work for his thesis was done at the Max-Planck Institute for Polymer Research courtesy of an informal exchange program between Prof. Lenz and Professor Gerhard Wegner. Since 1990, he has been employed as a chemical engineer specializing in conducting polymers and nonlinear optical polymers with the Chemistry and Materials Branch at the China Lake Naval Air Warfare Center. He has 45 publications, 10 patents and a second degree Black Belt in Songahm Taekwondo.

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AEROSPACE FINISHING SYSTEMS FOR NAVAL AVIATION

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ABSTRACT

Finishing systems on Navy aircraft perform a variety of functions, but clearly the most critical of these is the protection of aircraft structures from environmental degradation. Protective coatings serve as the primary defense against corrosion of aircraft metallic alloys, as well as degradation of other materials such as polymeric composites. Traditional coatings for aircraft include inorganic pretreatments, epoxy primers and polyurethane topcoats. Pretreatments provide some corrosion protection and prepare the surface for subsequent organic coatings. Primers normally contain high concentrations of corrosion inhibitors, such as chromates, and they are designed to provide superior adhesion and corrosion protection. Polyurethane topcoats are formulated to enhance protection and durability; they also provide desired optical effects (i.e., aesthetics or camouflage). More recently, alternative coatings have been developed, such as non-hexavalent chromate pretreatments, self-priming topcoats, flexible primers, low volatile organic compounds (VOC) content coatings, temporary and multi-functional coatings. These new developments reflect trends in protective coatings technology, changes in aircraft operational requirements/capabilities, and, most dramatically, concerns over environmental protection and worker safety. These environmental issues have created a drive toward coatings with ultra low (possibly zero) concentrations of VOC and non-toxic corrosion inhibitors. In turn, these changes have led to concerns over long-term performance, especially protection against corrosion. This paper reviews current protective coatings technology for Navy aircraft structures and discusses future needs and trends based on advancing technology, environmental concerns, and operational requirements.

KEY WORDS: Aircraft coatings, pollution prevention, inorganic pretreatments.

INTRODUCTION

Coating systems on Navy aircraft perform a wide variety of functions: They provide desired optical effects (i.e., aesthetics, camouflage), corrosion prevention, erosion control, markings, electrical grounding, electromagnetic shielding, as well as other specialized properties. Clearly, their most critical contribution is the protection of materials and structures from corrosion and other forms of environmental degradation. An Air Force study (1) concluded that, "The rate controlling parameter for the corrosion of aircraft alloys, excluding the mechanical damage factor, is the degradation time of the protective coating system." These coatings protect not only metallic alloys from corrosion, but also plastics and polymeric composites from various degradation mechanisms (2). Specifically, Navy aircraft are deployed at coastal land bases or onboard aircraft carriers. The continuous proximity to salt water and high humidity combined with atmospheric impurities cause one of the most corrosive natural environments. In addition, many operational and maintenance chemicals commonly used or found on aircraft, such as paint strippers, battery acid, de-icing fluids, and cleaners, are corrosive. These effects are exaggerated even more so with aging fleet aircraft that have flown many flights over long periods of time, adding fatigue as another factor. Considering the high cost of these aircraft, in addition to fewer numbers of new aircraft programs, aircraft materials protection is of the utmost importance.

The most common organic coating system applied to the exterior surfaces of Navy aircraft consists of an inorganic pretreatment, an epoxy primer and a polyurethane topcoat. In addition to this primer and topcoat paint system, other technologies have been introduced such as flexible primers and self-priming topcoats. These coating systems have protected aircraft structures from the frequently harsh operational environment due to their exceptional corrosion inhibition, adhesion, and durability characteristics.

Unfortunately, these coating systems have been identified as a major contributor to the generation of hazardous materials and hazardous waste for the DOD (3). Recently, changes in coating composition and application procedures have occurred because of these concerns for environmental protection and worker safety. Many of these coatings have contained high levels of volatile organic compounds (VOC) as solvents and plasticizers, and heavy metal compounds as corrosion inhibitors and colorants. These ingredients are being severely regulated and coating formulations are being drastically changed accordingly. These environmental issues have created a drive toward coatings with ultra low (possibly zero) concentrations of VOC and non-toxic corrosion inhibitors.

Nonetheless, corrosion protection remains a primary requirement and therefore these changes have led to concerns over long term performance. The practical lifetime of these coatings is 4 to 8 years, after which the coating system is removed. The aircraft surface is then cleaned, pretreated, and repainted. References (4-8) provide more information about general aircraft finishing systems. The following is a description of the specific finishing systems being used on Navy aircraft and future trends in these materials.

STANDARD FINISHING SYSTEMS

Surface Pretreatments   The primary goal of surface preparation and pretreatment processes is the enhancement of the corrosion resistance and adhesion properties of subsequent organic coatings. Proper surface preparation is an important step in the protective treatment of aluminum, and is accomplished by using materials such as alkaline cleaners, etchants and deoxidizers. These materials remove organic contamination along with the existing surface oxide layer of the aluminum to prepare it for subsequent chemical pretreatments. These pretreatments are used because of their enhancement of the overall protective finishing system. MIL-S-5002 "Surface Treatments and Inorganic Coatings for Metal Surfaces of Weapon Systems" is the military specification for surface preparation and pretreating of virtually every Navy aircraft and weapon system. The two primary surface pretreatments for aircraft are chromate conversion coatings and anodic films. Chromate conversion coatings (CCC) are excellent surface pretreatments for aluminum alloys. These materials chemically form a surface oxide film (typically 40-60 mg/ft^2), which enhances the overall adhesion and corrosion prevention properties of the protective finishing system applied over them. Typical CCC film performance requirements are covered by MIL-C-5541 "Chemical Conversion Coatings on Aluminum and Aluminum Alloys" and CCC material properties are described in MIL-C-81706 "Chemical Conversion Materials for Coating Aluminum and Aluminum Alloys." Anodize processes form a thicker oxide film (200+ mg/ft^2) by electrochemical means, which provides more protection against degradation than chemical conversion coatings.

Primers   Epoxy resins are commonly used as binders in high performance primers due to their exceptional adhesion and chemical resistance properties. The solvent-borne epoxy primer is manufactured and packaged as a two component epoxy/polyamide system. One component contains an epoxy resin which is the product of a condensation reaction between epichlorohydrin and bisphenol A. The second component is a solution of a multifunctional polyamide resin in a solvent blend. Upon mixing the two components, which is done just prior to application of the primer, reaction of epoxide and amide groups within the resins ensues:

$$\underset{\text{R}-\text{CH}-\text{CH}_2}{\overset{\text{O}}{\triangle}} \; + \; \underset{\text{R}'-\text{C}-\text{NH}_2}{\overset{\text{O}}{\|}} \; \longrightarrow \; \underset{\text{R}-\text{CH}-\text{CH}_2-\text{NH}-\text{C}-\text{R}'}{\overset{\text{OH}\qquad\qquad\qquad\text{O}}{|\qquad\qquad\qquad\|}}$$
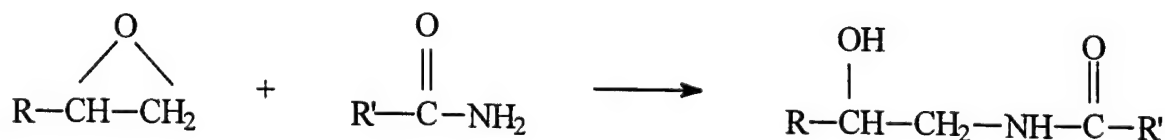
The product of this reaction is a highly crosslinked polymer which forms the matrix of the primer film. The chemical and mechanical properties of the epoxy matrix cause the primer to be adherent, chemically resistant, and durable. Hydroxyl groups on the solid epoxy are usually given credit for the excellent adhesion of these coatings. References (9) and (10) provide detailed discussions of epoxy resin chemistry for coatings.

The epoxide component of the primer contains various pigments, including titanium dioxide, strontium chromate, and extender pigments. Strontium chromate is the most critical of these pigments since it is well known as an exceptional corrosion inhibitor,

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especially for aluminum. Titanium dioxide in the primer enhances durability, chemical resistance, and opacity of the applied coating. The extender pigments can be silicas, silicates, carbonates, or sulfates. The extenders are normally inexpensive and provide a cost effective component which "fills" the coating and reduces gloss of the applied film. The surface irregularities which cause gloss reduction also act as anchors for a topcoat, thus enhancing inter-coat adhesion by improving the mechanical attachment. References (6) and (7) provide a comprehensive review of epoxy primer technology for aircraft applications.

Upon mixing the two components of the epoxy/polyamide primer, the curing reaction begins. At this stage, the coating is suitable for spray application. After application of the coating to a dry film thickness of 15 to 24 microns (0.6 to 0.9 mils), the coating is tack-free within 1 to 5 hours and dry hard within 6 to 8 hours. For corrosion-prone areas, the primer may be applied up to double this thickness. If a topcoat is to be applied, it is usually accomplished within the tack-free to dry hard time period to ensure proper adhesion. The primer attains sufficient dry film properties within 7-14 days of application.

Since water is a primary factor in reducing adhesion of paint films and causing cathodic disbondment, adhesion is considered a critical paint performance property. Adhesion of the primer is characterized by a tape test after a 24 hour immersion exposure period in distilled water (11). The required performance is no coating removal from the substrate. Adhesion is also characterized by a method which quantifies the force required to scrape the primer from the substrate (12). Typically scrape adhesion values of at least 3 kg is considered acceptable. Other adhesion tests employed in research and development laboratories are the tensile adhesion and Hesiometer knife-cutting adhesion tests (13). These sophisticated laboratory adhesion tests yield quantitative data but require more training and expertise to perform the tests and to analyze data compared to the tape and scrape adhesion tests.

Corrosion resistance is evaluated by applying the primer to chromate conversion coated aluminum substrates such as 2024 T3. After curing for 7-14 days, the primer is scribed with an "X" so that the substrate is exposed. Resistance to 5% NaCl salt fog exposure is required such that no substrate corrosion or coating defects are produced after 2000 hours of exposure. Resistance to filiform corrosion is evaluated on primed and top-coated test panels. After exposure to hydrochloric acid for one hour, the panels are exposed to high humidity for 1000 hours. Generally, specimens should not exhibit filiform growth from the scribe greater than 3.175 mm (0.125 in). In addition to the salt fog and filiform tests, the Navy also requires the corrosion resistance of primed and then scribed aluminum/graphite epoxy specimens. This forms a galvanic couple which must withstand 5% NaCl salt fog exposure for 500 hours such that pitting greater than 1 mm (0.039 in) is not produced. SO_2/salt fog exposure and electrochemical impedance spectroscopy have also been used to evaluate the corrosion resistance properties of coating systems.

The high-performance waterborne epoxy primer that is currently used on exterior surfaces of many military aircraft was developed (14) and implemented in the Navy community in the late 1970's to mid 1980's. This primer is supplied as a two-component epoxy/amide or epoxy/amine system. The resin systems are water-reducible, and film formation occurs via coalescence of resin particles and crosslinking of the epoxy/polyamide reactive groups.

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The pigments used are similar to those used in the solventborne primer system. For example, strontium chromate pigment is used as the primary active corrosion inhibitor in many waterborne primers. Organic co-solvents and surface active agents are also used to enhance formulation and processing properties such as water miscibility and dispersion stability, as well as film formation and quality.

The epoxy primer is brittle, especially at low temperatures (-51°C), which can potentially result in extensive cracking of the paint system in highly flexed areas of the aircraft. Sealants, which are sometimes spray applied between the primer and topcoat in aircraft finishing systems, to increase overall coating system flexibility, are soft, easily deformed, and difficult to apply and remove. An alternative is an organic coating that possesses the adhesion of a primer and the flexibility of a sealant, thus eliminating the logistical and application problems inherent in stocking and applying two materials instead of one. An elastomeric primer which provides these benefits has been characterized (15) and implemented on Navy aircraft. This material is based on polyurethane resin technology, and a pigment system which contains strontium chromate for corrosion inhibition, and extender pigments for gloss control. Most of the requirements for this flexible primer are similar to those in the current epoxy primer specifications, with the exception of film flexibility. This requirement is significantly more stringent than those exhibited by the current epoxy primers: 80% versus 10% room temperature elongation, respectively. One of the major coating failure mechanisms on aircraft is cracking around fasteners, thus exposing bare metal. Application of this coating to numerous Navy and Air Force aircraft has resulted in less coating system failures due to cracking and chipping.

Topcoats A high-performance topcoat is applied to Navy aircraft in order to enhance protection against the operational environment and to provide desired optical properties. Aliphatic polyurethane coatings are ideal for this application due to their superior weather and chemical resistance, durability, and flexibility. These urethanes are two component, reactive materials. One component of the coating is a polyisocyanate resin or an isocyanate terminated prepolymer based on hexamethylene diisocyanate (HDI). The second component contains a hydroxylated polyester. Upon mixing, the isocyanate groups react with the hydroxyl groups of the polyester:

$$R-N=C=O \quad + \quad R'-OH \quad \longrightarrow \quad R-NH-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-O-R'$$
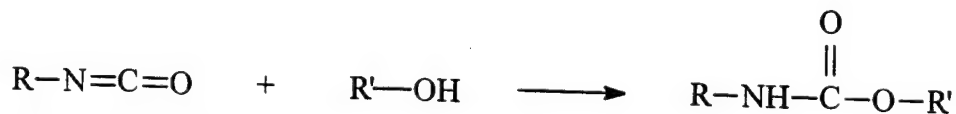
The resulting polymer is flexible yet extremely durable and chemical resistant. Aliphatic isocyanates and polyesters are used in topcoats because they provide outstanding weather resistance compared to epoxies, whose aromatic groups degrade when exposed to ultraviolet light. References (16-19) provide more detailed discussions about polyurethane chemistry.

When the two components are combined and the polyurethane reaction begins, the coating is ready for application (i.e. no induction time is required). This coating is normally spray applied to a dry film thickness of 50.8 ± 7.6 microns (2.0 ± 0.3 mils). The typical topcoat is

set-to-touch and dry hard (when cured at room temperature) within 2 and 8 hours, respectively. Although the painted surface can be handled after 6 hours without damage to the coating, full performance properties are normally not obtained until approximately 7-14 days.

The most critical performance requirements for topcoats are weather resistance, chemical resistance, and flexibility. Weather resistance is evaluated by laboratory exposure in an accelerated weathering chamber (20) for 500 hours. This chamber is a continuous cycle of high intensity ultraviolet light (xenon arc) and water spray. Although studies have shown that there is no precise correlation with outdoor exposure (21-23), the accelerated exposure does indicate if the coating is susceptible to ultraviolet and/or water degradation. These results are used in conjunction with actual outdoor exposure for 1 year. Both accelerated and real-time weathering conditions cause only minimal changes in the color, gloss, and flexibility of high performance aircraft topcoats.

Chemical stability is evaluated by exposure of the applied topcoats to various operational fluids such as lubricating oil, hydraulic fluid, and jet fuel at elevated temperatures and/or extended durations. Aerospace topcoats are also subjected to a dry heat of 121°C (250°F) for one hour. Suitable topcoats show no defects other than slight discoloration after exposure to these conditions.

Flexibility requirements for polyurethane topcoats include impact and mandrel bend tests. For high gloss colors, a 40% elongation of the coating after impact at room temperature and a 180° bend around a 2.54 cm (1.0 in) cylindrical mandrel at -51°C (-60°F) are required without cracking of the film. Flexibility requirements for low gloss colors are less stringent at low temperatures, since it is difficult to formulate flexible low gloss coatings due to high pigment concentrations, which normally embrittle the film.

Self-Priming Topcoat   The self-priming topcoat (SPT) is a VOC compliant, non-lead, non-chrome high-solids polyurethane coating that was designed to replace the current primer and topcoat paint system used on aircraft (24). The SPT possesses the adhesion and corrosion inhibition properties of a primer as well as the durability and optical properties of a topcoat. The SPT effectively eliminates the need for a primer and thus eliminates the application man-power, time, and materials. In addition, the hazardous emissions and toxic wastes that are associated with current aerospace primers are eliminated. SPT's have been successfully applied to a full variety of operational Navy aircraft (i.e., F-14, F-18, AV-8, H-3, H-46, P-3).

Specialty Coatings   In addition to the current primers, topcoats, and self-priming topcoats used on the exterior surfaces of Navy aircraft, other specialized coatings are utilized to address specific concerns.

Sealants   Although the current epoxy primers provide excellent adhesion and corrosion inhibition, they are brittle. This lack of ductility may result in cracking of the paint system on highly flexed areas of the aircraft. In order to improve the overall flexibility of the epoxy primer polyurethane topcoat coating system, sealants are frequently incorporated into aircraft finishing systems. These sprayable materials are applied between the primer and the topcoat at thicknesses up to 203 microns (8 mils) and are primarily formulated

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from polysulfide, polyurethane, and polythioether binders. Their elastic nature minimizes cracking of the paint system. Critical requirements in these specifications are low-temperature flexibility (mandrel bend tests), chemical resistance (fluid immersion at elevated temperatures), and corrosion resistance (5% NaCl salt spray tests). Although these sealants provide corrosion protection by the formation of a relatively impermeable barrier, some sealants also contain strontium chromate for chemical corrosion inhibition. A detailed discussion of this technology can be found in references (25, 26).

Rain Erosion Coatings In addition to their harsh environment, aircraft must also endure seemingly harmless natural conditions that can deteriorate the performance of coatings and their underlying structures. One example of this phenomenon occurs when airborne debris, such as sand or rain droplets, impact aircraft leading edges and radomes during flight. The force of impact from these particles can erode the coating system and adversely affect the underlying substrate. The current primer and topcoat, and SPT paint systems do not provide adequate protection against this condition. Even when applied at two to three times its normal thickness, the coating system erodes prematurely.

The rain erosion-resistant coating used on Navy aircraft is a two component polyurethane material. One component consists of a pigmented high molecular weight polyether type polyurethane. The other component contains a clear ketimine (blocked diamine) resin that acts as both a crosslinking agent and a chain extender. When combined, the two components form an elastomeric coating which can absorb and dissipate the energy of impacting rain droplets, thus preventing failure. Flexibility is characterized by a 0.635 cm (0.25 in) mandrel bend at -51°C (-60°F) and tensile elongation of 450%, whereas the standard topcoat only requires a 2.54 cm (1.0") or 5.08 cm (2.0") mandrel and elongation of 10 or 40 %. However, in order to exhibit this high elasticity, the polymer crosslink density is decreased causing reduced chemical resistance and weathering properties. In order to improve the finishing system durability, these materials are normally overcoated with the standard topcoat.

Although elastomeric coatings offer increased resistance to rain erosion, the optimum protection for Navy aircraft is provided by elastomeric tapes. These materials can be clear or pigmented, polyurethane based films and are supplied with or without an adhesive backing. Unlike coatings, these tapes are bonded to the surface and do not require a drying time. Early versions of these materials were clear aromatic type polyurethanes. Although durable, these aromatic materials had poor weatherability. The latest versions of these materials, however, are aliphatic. These new materials are extremely durable and have excellent weatherability.

High Temperature Resistant Coatings Various areas of Navy aircraft are routinely subjected to elevated temperatures during operation. The standard paint system was only designed to resist thermal exposures up to 176°C (350°F) for short durations. Therefore, two types of materials are employed for application in these areas: ceramic coatings and high temperature resistant silicone based coatings. Since ceramic coatings are beyond the scope of this review, they will not be discussed. Typical high temperature silicone based coatings use aluminum pigment and are designed to withstand temperatures up to 650°C (1200°F). They can be applied by conventional air spray and are cured by heating to

204°C (400°F) for 1 hour or upon elevated temperature exposure under component operation. During the curing period, the binder system for this coating will oxidize, leaving a barrier layer of silicone oxide/aluminum to protect the underlying substrate from adverse conditions. Although this material provides adequate barrier protection in the high temperature range, the performance diminishes dramatically in the mid-temperature range (260 to 370°C, 500 to 700°F) or when damaged.

Fuel Tank Coatings Certain internal areas of aircraft are exposed to selective environments which pose unique problems. One example is fuel tanks. Aviation fuels contain additives which may be corrosive. If left unprotected, fuel tanks would corrode and leak. In order to protect these areas, epoxy or polyurethane fuel tank coatings are used. These highly cross-linked, chemically resistant coatings are two component materials designed for application to non-ferrous surfaces. The fluid resistance requirements for this material are significantly more severe than those of the standard primer and topcoat. The conventional topcoat must withstand 24 hour immersion on unscribed panels without degradation, whereas the fuel tank coating specification requires 14 days immersion of specimens with scribes through the coating. This high degree of chemical resistance is necessary because the coating is not only subjected to the various chemicals contained in aviation fuels, but it is also exposed to aircraft operational chemicals, salt water and dilute acidic solutions (27).

COMPLIANT COATINGS ISSUES AND FUTURE TRENDS

Environmental Regulations And Hazardous Materials As the environmental consciousness of the world continues to increase, more efforts are being devoted to finding safe, compliant solutions to past, current, and future environmental problems. One major factor affecting the Naval Aviation in recent years, has been the Clean Air Act Amendment (CAAA) of 1990. This law significantly affects the type of materials and processes which will be approved for use in the future. In response to this situation, the Navy has expanded its efforts to reduce the amounts of hazardous materials generated from the cleaning, pretreating, plating, painting and paint removal processes used in both production and maintenance operations. The materials associated with these processes have been identified as major sources of hazardous waste by the EPA (28). Specifically, numerous research and development efforts have been established to address the environmental concerns with organic coatings. These environmental efforts can be described by two main thrusts: the development of low volatile organic compound (VOC) coatings, and the development of non-toxic inhibited coatings. The efforts in low VOC are aimed at reducing the volatile organic compound content of aircraft coatings to meet environmental regulations, especially the state of California's Air Quality Management Districts (AQMD) rules and the CAAA Control Techniques Guideline (CTG) for the aerospace industry (one of 174 source categories). The development of non-toxic inhibited coatings is concerned with eliminating toxic heavy metal pigments, such as lead, chromates and cadmium used in protective primers and topcoats.

Low VOC versions of the standard military aircraft primers and topcoats have already been developed to comply with the CAAA Aerospace CTG. These materials are based on water-borne and high solids. Exempt solvents technology, while solving a VOC problem in most

cases, creates an ozone depleting chemical problem and is no longer perceived as a potential technology solution.

Non-Chromated Pretreatments   One of the main environmental thrusts in the pretreatment area is the total elimination of hexavalent chromium. This toxic material has been used widely in the aforementioned processes because of its outstanding performance as a corrosion inhibitor for aluminum. This property is of particular importance to the Navy due to the extensive use of aluminum in aircraft and weapon systems. Chromium VI is a known carcinogen, and regulatory agencies have recently enacted rules which limit or prohibit the use of this material. This has resulted in a need for alternative materials to be developed.

Non-chromated alkaline cleaners and non-chromated deoxidizers have been identified as acceptable alternatives to the current chromated processes, and have been implemented by Naval facilities. These materials have provided satisfactory performance in these surface preparation operations and in some cases they have been more cost effective than their chromated predecessors.

Numerous non-chromated surface pretreatment materials have been investigated as replacements for the standard chromated conversion coating (CCC). A summary of one such investigation is described in Reference (29). Three categories of non-chromated conversion coating alternatives have been studied in the Navy: inorganic non-chromated solutions, chromium (III)-based treatments, and sol-gel formulations. The first category includes solutions based on permanganate, cobalamine, and ceric ion (among others) as the active corrosion-fighting agent. At this time, the performance of these materials is marginally comparable or inferior to conventional CCCs in adhesion and corrosion resistance. A Navy-developed chromium (III) treatment (30,31) has shown corrosion resistance and paint adhesion properties comparable to CCCs in laboratory evaluations; broader testing and in-service demonstrations of this technology are underway. Sol-gel formulations, although still in the initial phases of development, show promise for favorable conversion coating properties. These materials are organic/inorganic polymers based on the hydrolysis and condensation of metal alkoxides. The drawing below illustrates how, for example, silicon alkoxides (of general formula $Si(OR)_4$) can be reacted to form a barrier film strongly bonded to an oxidized aluminum surface:
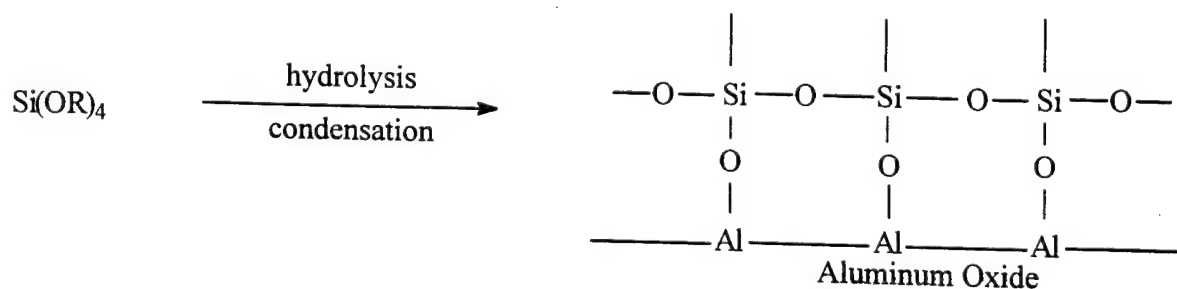
The chemistry of sol-gel films also allows a great deal of flexibility in modifying adhesive and other properties. While some of these alternatives have shown promise, an across-the-board replacement for chromate conversion coatings has not yet been achieved.

Chromic acid anodizing (CAA) has been widely used in aerospace production and maintenance operations. Typical performance requirements for this type of film are described in MIL-A-8625 Type I "Anodic Coatings, for Aluminum and Al Alloys." However, due to the increasing restrictions on hexavalent chromium, several potential alternatives have been identified. These alternatives are: sulfuric/boric acid anodize (SBAA) and thin film sulfuric acid anodizing (TFSAA), as well as the standard Type II sulfuric acid anodizing. General information on these processes can be obtained from References (32-35). Several Navy Laboratory investigations were performed on these alternatives as described in references (36-38). After a full scale successful demonstration of SBAA at the Naval Aviation depot at North Island NAS, it has been approved for use and incorporated into the MIL-A-8625 specification as Type IC (sulfuric/boric acid anodize). Also, the laboratory studies have resulted in the definition of acceptable performance parameters for the thin film sulfuric acid anodizing alternative which was incorporated into MIL-A-8625 as Type IIB.

Waterborne Technology Water has long been used as a carrier for organic coatings. The polymers for these coatings are usually modified with hydrophilic groups and dispersed in water to form either solutions or emulsions. Most latex paints are based on thermoplastic resins which are suspended in water to form spherical particles. These particles, whether pigmented or neat, are usually covered with a thin layer of emulsifier to maintain a stable dispersion. When applied to a surface, these spheres coalesce into a continuous film as the water of the emulsion coating evaporates. This film formation mechanism tends to lead to longer drying times in high humidity environments. Other effects of using water as the diluent include: smoother surface finishes due to greater flow times, less overspray when using air application equipment (due to the higher density of water), and easier clean up (usually accomplished with soap and water). Unfortunately, these coatings have some disadvantages. For example, they are more sensitive to surface contamination, like oils and greases. Also, these films tend to be porous and their high affinity for water can lead to poor resistance in moisture environments resulting in coating failure when wet, or exposed to high humidity conditions.

Waterborne or water-reducible, high-performance coatings are unique in the way that they contain resins which are usually not soluble in water. The resin exists in its own micellar phase. Because the polymer exists in its own organic phase surrounded by water, the solvent distributes between the organic phase and the aqueous phase. This solvent, called the coalescing solvent or co-solvent, aids in film formation as the water evaporates by allowing binder and pigment particles to fuse in a continuous film (39). Since water is used as the primary liquid medium or as a diluent, formulations based on waterborne resins have much lower VOC levels than their solventborne counterparts. Recent advances in urethane technology have shown that coatings approaching zero VOC are feasible, consisting of low viscosity, water-soluble reactants (40).

Polyurethane coatings are an area where high performance water-borne coatings have been investigated. One-component polyurethane dispersions have been in existence for some time and generally consist of fully reacted polyurethane resins which are predominately thermoplastic. Since urethanes are not readily compatible with water, these systems are modified ionically and non-ionically with hydrophilic groups to aid in the stability of the dispersions. After application, these films form by the coalescence of the long chain urethanes. Although some work has been performed to investigate ways of crosslinking these systems, they tend to have lower crosslink densities and are not as chemically resistant as their solvent-borne counterparts.

Recently, resin manufacturers have shown signs of success in working with two component water based polyurethane resins for high performance coatings. One example is based on an aliphatic polyol prepolymer and a polyisocyanate. The polyols are prereacted with a di-isocyanate and emulsifying agents to form a linear hydroxy-terminated prepolymer. The hydroxy-functional groups aid in the stabilization of the polyurethane dispersion. In addition, a water dispersible polyisocyanate has been synthesized which has a preferential affinity for the polyol over the water competitor. The two components are mixed with an excess of isocyanate to form the final high performance polyurethane product. Other variations on water based urethane chemistry are being investigated by the commercial resin industry, and coating's manufacturers have begun to formulate finished products from this technology.

High Solids Technology Another method to attaining a lower VOC coating is through the use of high solids technology. Several paths to increase coating solids are possible. The first and most obvious reduction comes from simply lowering the solvent concentration. While this approach reduces the VOC content, it shortens the pot life and significantly increases the resin viscosity when traditional raw materials are used. Also, the surface finish tends to be rougher from decreased flow characteristics. Another option to lower VOC is through the use of reactive diluents such as neopentyl glycol, diglycidyl ether (NGDE). These materials are low molecular weight compounds which act like a solvent for viscous resins. On curing, the reactive diluent becomes part of the polymer backbone; it is not driven off as a VOC. Using low molecular weight resins can produce a high solids coating with lower viscosity and better flow properties. However, these materials tend to have shorter workable pot lives and lower flexibility when cured with traditional polyisocyanates. This lower flexibility is related to the increase in crosslink density resulting from the smaller backbone structures between functional groups. Using narrow molecular weight distribution isocyanate terminated prepolymers as the isocyanate source produces low VOC coatings with good performance and processing characteristics. These prepolymers yield coatings with lower viscosity, shorter drying time, and longer pot life.

A third approach is to use blocked polymers which yield a longer pot life, but they tend to be less mobile with slower reaction rates. Their decreased reactivity leads to long drying times, which is not desirable. Finally, high-boiling solvents can be used to replace convention solvents. By incorporating these materials, the applied films retain the solvent longer giving smoother surface finishes. However, this solvent retention leads to longer drying times and can allow the coating to continue to flow. This characteristic has

produced a new phenomenon where sharp edges can be exposed with time. Finally, solvent retention can result in eventual porosity in the film, decreasing chemical resistance properties.

In summary, each individual approach has identified deficiencies which present a challenging problem to resin companies. However, a combination of these technologies appears to have the greatest potential for success and is being pursued by numerous manufacturers. Several aerospace coating specifications have been developed based on this technology.

Low VOC Technology Status   Numerous military and commercial specifications have been written to cover materials based on these technologies. However, in light of the proposed CTG and the ozone depleting substances problem, these material specifications are currently being modified to eliminate the type allowing exempt solvents and all other non-compliant versions. This will authorize only low VOC materials for use. High performance VOC compliant primers, topcoats, and self-priming topcoats are required to have a maximum VOC content of 340, 420, and 420 g/l, respectively.

Waterborne and high-solids technologies have allowed for the development of protective coatings which contain a significantly reduced amount of VOC; some of these are currently under evaluation both in the laboratory and in the field. Novel polymeric resins suggest that the development of zero-VOC coatings, which meet or surpass all existing requirements, is plausible and should be available within the next five years.

Non-Toxic Inhibitive Primer   Until recently, chromates were virtually the sole source for active corrosion inhibition in aircraft coatings. This was due to their outstanding performance in protecting nearly all metals in a large range of environments. However, chromates have been shown to be carcinogenic, and their use and disposal are becoming severely restricted. This has led to much research and development of non-toxic inhibitors for use in coatings, including those for aircraft. Pigments which have been investigated as alternatives include phosphates, borates, molybdates, nitrates, and silicates.

The mechanisms by which these inhibitors perform have not been thoroughly defined. Proposed mechanisms for zinc phosphate include the adsorption of ammonium ions, complex formation on the exposed surface, passivation through a phosphating process, and anodic/cathodic polarization. Phosphates, borates, and silicates are generally regarded as anodic passivators which reduce the rate of corrosion by increasing anodic polarization. Molybdates also have been classified as anodic inhibitors and especially effective at inhibiting propagation of pits. At high concentrations, the oxidizing action of molybdates is the main factor behind its corrosion inhibiting ability. Molybdate ions migrate into anodic areas and accumulate there, especially in pitted areas. Although these pigments individually provide some level of corrosion inhibition, in general, one for one substitution for chromates has not resulted in coatings with equivalent corrosion prevention capabilities. However, synergistic effects from combinations of some inhibitors provide nearly equivalent or superior properties to chromates (35, 41-43).

Current available primers are based on 2-component high solids or water-borne epoxy systems and corrosion inhibitors such as molybdates, nitrates, borates, silicates, and/or

phosphates as well as a variety of metal cation systems. These primers have shown promise in general corrosion resistance and adhesion tests. However, most of these primers have had problems providing adequate filiform corrosion resistance. In addition, many of these experimental coatings have exhibited flexibility, strippability, viscosity and storage stability deficiencies. Further investigation of these materials is being conducted to alleviate these problems. Finally, a better understanding of the corrosion inhibiting mechanisms associated with these non-toxic inhibitors, both individually and as multiple inhibitor systems, needs to be attained to formulate corrosion preventive primers more effectively and efficiently.

Touch-up Paints   One approach which has been used to reduce VOC and hazardous waste from painting operations has been the development of self-contained touch-up paint applicators. One experimental kit contains approximately 10 cc of the base and curing agent in a clear, plastic tube separated by an impermeable barrier. When the barrier is displaced, the two components are easily mixed by shaking. A brush on the end is used to dispense and apply the mixed material. This kit can be used to touch-up areas of 1-2 square feet and has a number of advantages over spray application techniques:

1.   The small, touch-up kit restricts maintenance personnel from mixing large quantities of paints which may be applied to excessive areas or disposed of as a hazardous waste.

2. Brush application minimizes airborne concentrations of the toxic solvents, isocyanates, etc. in paints. Other personnel can work nearby without protective equipment.

3.   The individual components are premeasured to assure precise mixing and optimum properties.

Adhesive Films   Another approach to avoiding VOC from painting operations involves replacing the topcoat altogether, using adhesive appliqué films. One of the primary means of protecting aircraft radomes and leading edges from rain-erosion is the use of elastomeric tapes. These are flexible films bonded to painted surfaces with an attached adhesive. These adhesive films provide a durable, weather-resistant finish when applied over standard, corrosion-resistant primers. The films can be formulated from polyester, polyurethane, or fluorocarbon resins with acrylic or other adhesives. Application of these films can be done in any enclosed area with minimal training. Nearby personnel can do installation and maintenance work at the same time, since no safety or environmental hazards are present.

Electrodeposition Coatings And Powder Coatings   Electrodeposition of paint works on the same principle as chrome plating of metal. Charged paint particles are electrically plated to an oppositely charged conductive substrate. The object to be coated is dipped into the electrodeposition tank and the current is turned on. This causes the paint solids to deposit onto the substrate as a paint film. During the operation, the paint coats every conductive surface, regardless of shape, with a uniform film whose thickness can be controlled very accurately. The paint film then insulates the substrate, preventing any further deposition of the coating. More detailed descriptions of the electrodeposition (e-coat) process can be found elsewhere. (44-46)

Because waterborne coatings are used in the e-coat process, VOC are kept to a minimum. Also, no flammability hazards exist and no elaborate ventilation systems are required, as with conventional spray techniques. A significant hazard does exist, however, with the enormous power required. The tank area must be enclosed and have fail-safe controls. The technique is also limited to small, conductive parts in aircraft applications. Also, typically temperatures around 149°C (300°F) or more are required for cure of these coatings.

Powder coatings can be applied by a variety of methods, including dip coating-fluid bed; electrostatic dip coating-cloud chamber; and the most ideal, spray-electrostatic spray. With electrostatic spray, as the powder passes the high-voltage electrode at the tip of the spray gun, it picks up the electrostatic charge and is attracted to grounded work. There, the powder adheres and will remain until fused and cured in an oven. More detailed descriptions of powder coatings and application techniques can be found in the literature. (45,47)

As with e-coats, film thickness of powder coatings is controlled by the insulating effect of the powder film as it builds up on the substrate. Overspray is considerable, but it can be collected and reused, so losses are low. Because the material is a solid, there are no VOC, but an explosion hazard potential exists due to the fine dust overspray. Therefore, careful grounding of the booth and all equipment is required.

Small parts which have been primed with an e-coat and topcoated with a powder coating exhibit outstanding protective properties due to the excellent barriers produced by both application technologies.

Paint Application Equipment As part of the CAAA Aerospace CTG, conventional air spray application equipment will no longer be authorized for applying paints. Conventional air spray equipment has a transfer efficiency of approximately 28%. The types of paint application equipment authorized for these materials will be similar to those specified by the State of California's AQMD Regulations which require minimum transfer efficiencies of 60% to 85% and maximum gun tip air pressures of 10 psi. A number of alternative technologies have been proposed to meet this requirement. The only two spray application techniques authorized will be electrostatic and high-volume low-pressure (HVLP) spray guns. Both of these techniques have improved transfer efficiencies over conventional air spray. Roller, brush, dip and other non-spray methods are also acceptable. Each of these techniques has its own unique capabilities and limitations. Some methods can be used in combination (i.e. plural component, air-assisted airless with electrostatic) to yield even higher efficiencies.

The method of cleaning spray equipment is also being regulated under the CTG. The old solvent wash method, which generated large quantities of hazardous waste and was time consuming, is being prohibited. Some type of enclosed cleaning method, which captures the majority of the cleaning solvent, has to be used. Paint gun washers that meet this requirement have been identified. In addition to drastically reducing the solvent emissions, these enclosed cleaning operations take approximately one fourth of the working time as compared to the old method.

SUMMARY

Many new innovations in protective coatings technologies have emerged during the past few years. Some of these include: corrosion sensor, pressure sensitive, preferentially strippable coatings, and decal technology. However, the biggest driver in coatings research and development has been and will continue to be the continuous implementation of more stringent environmental regulations which limit the types and amounts of materials used in coatings formulation and application processes. These mainly affect volatile organic compounds and heavy metals, although other types of chemicals have come under scrutiny. These regulations are causing dramatic changes in how coatings are formulated as well as the raw material from which they are derived. Research and development of low VOC polymer systems (i.e., high solids, waterborne, powder coatings, etc.) and non-heavy metal compounds will continue well into the next century and the advances from these fundamental efforts will be translated to changes in coatings technology. In addition, the approach to improve aircraft finishing system performance will be attained through investigation and utilization of high performance polymers, pigments, and additives.

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21st CENTURY AIRCRAFT DEPAINTING STRATEGIES

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ABSTRACT

Current chemical paint strippers for aircraft contain toxic and hazardous components and depainting operations are a major source of hazardous waste generation in the DOD. Federal and state agencies have begun to restrict the use of these hazardous materials and Government directives require significant reductions in hazardous waste generation. The Naval Air Systems Team (Laboratories, Depots and Headquarters) has teamed with the Air Force at Warner Robins Air Logistics Command in investigating advanced paint removal technologies and has taken a multi-process approach to meeting the requirements of aircraft and component stripping at various levels of maintenance. This paper describes the results of development and application of current and emerging technologies which can be used safely on aircraft metallic or composite surfaces.

KEY WORDS: Aerospace/Aircraft, Paint Removal, Cleaning

1. INTRODUCTION

During the life cycle of military aircraft, paint stripping and recoating are required periodically for inspection, maintenance and repair as well as for changes in paint schemes and special purpose coatings. Over 1000 rotary and fixed wing aircraft are stripped at the Naval Aviation Depots each year. Other military and commercial aircraft may similarly require stripping and repainting approximately every 3 to 7 years during their operating lifetimes. In the past, aircraft painted surfaces consisted primarily of aluminum alloys. In recent years, military and commercial aircraft surfaces are increasingly comprised of reinforced organic matrix composites, with different damage susceptibilities. The paint systems used on military aircraft over the last 25 years have included epoxy primers and polyurethane topcoats, which are more difficult to remove than the enamels and acrylics used earlier.

Historically the chemical paint strippers used on aircraft surfaces have been formulated with methylene chloride, which penetrates and attacks polymeric coatings quickly and effectively. To enhance the stripping of tough epoxy and polyurethane coatings, phenol activators were added. Chemical stripping with methylene chloride is labor intensive and

time consuming and frequently requires additional sanding and scraping, followed by extensive rinsing. Large quantities of hazardous waste are generated, requiring increasingly expensive treatment and disposal procedures. Methylene chloride (1) is a toxic organic compound which adds to the Total Toxic Organic (TTO) level in maintenance activity waste streams. The elimination of chemical stripping of aircraft with methylene chloride and phenols is encouraged by the Clean Air and Clean Water Acts, the Resource Conservation and Recovery Act (RCRA), and the National Emission Standards for Hazardous Air Pollutants (NESHAP).

2. ENVIRONMENTAL, SAFETY AND HEALTH REQUIREMENTS

Chemical paint stripping and the related processes of cleaning and repainting are among the most air polluting, wasteful and time consuming processes in aerospace maintenance and manufacturing. Figure (1) identifies the top source processes for hazardous air pollutant emissions from the aerospace industry. The contamination of intact paint primer layers during chemical paint stripping results in the unnecessary requirement to remove all of the damaged primer layer. The result is greater amounts of chemicals, waste and air emissions that result from reapplication of chemical paint strippers, rinsing, washing, rinsing, chemical conversion coating, rinsing, and in some cases repriming the aircraft prior to rework.
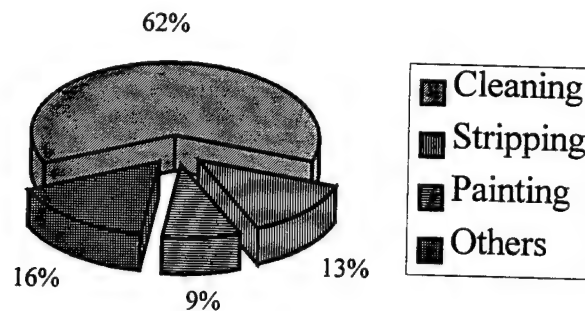
Figure 1. Aerospace Industry HAP Emissions by Source Process

2.1 Aerospace NESHAP As a result of the Clean Air Act and Amendments, a National Standard for Hazardous Air Pollutants (NESHAP) for Aerospace and Rework Facilities will become effective in September, 1998.

The Enviromental Protective Agency (EPA) has classified methylene chloride and phenol as hazardous air pollutants (HAPs). The standard for depainting operations at major source facilities specifies that no HAPs shall be emitted from chemical depainting operations with an exception for radomes, parts normally removed from the aircraft during depainting and for spot stripping or decal removal (2). If facilities choose to use mechanical means for depainting, there are operating requirements for depainting operations generating airborne inorganic HAP, including closely monitored control with particulate filters or waterwash systems. Sanding operations are exempt.

2.2 Hazardous Waste and EO 12856 The cost of hazardous waste disposal at some aircraft depots has increased by more than 100% over the last five years. Despite efforts to implement technology that complies with near term laws, most depots still pay in the range of $3M to $5M per year to dispose of hazardous waste. In most cases, depainting operations are one of the top three processes contributing to hazardous waste treatment and

disposal costs (3). By definition, any process that creates large amounts of waste is inefficient and, therefore, should be replaced or improved.

Executive Order 12856 requires a 50% reduction in toxic waste transferred off-site from federal maintenance facilities. In addition, the Order requires the use of pollution prevention strategies as the primary method to reduce toxic waste. The implementation of plastic media lease agreements has moved the cost of hazardous waste disposal to the media lease agreement. Since pollution prevention includes the substitution or elimination of the wasteful source process, the implementation of efficient, environmentally compliant and cost effective aircraft paint removal processes is a major economic, environmental and safety benefit for aerospace rework facilities.

2.3 OSHA PELs Extremely small quantities of airborne toxics in the workplace threaten to make accepted paint removal practices impractical. The Occupational Safety and Health Administration (OSHA) has set standards for Permissible Exposure Limits (PELs) for employees working with and around hazardous materials. The limits (Table 1) are based on a time weighted average for an eight hour period. Proposed new standards are listed in Table 2 with the resultant paint stripping materials or processes affected (4).

Table 1. Current OSHA Permissible Exposure Limits

Toxic Substance	Chemical Abstracts Number	Permissible Exposure Limit (PEL)
Cadmium	7440-43-9	$5.0\ \mu g/m^3$
Chromium	7440-47-3	$0.5\ mg/m$
Methylene Chloride	75-09-2	500 ppm

Table 2. Impact of Proposed OSHA Permissible Exposure Limits

Toxic Substance	Proposed (PEL)	Affected Processes
Cadmium	$5.0\ \mu g/m^3$	any dry media blasting
Chromium	$0.5\text{-}5.0\ \mu g/m^3$	any dry media blasting
Methylene Chloride	25 ppm	HAP chemical paint stripping, sealant removal and spot stripping

The expanded OSHA workplace standard for chromium will incur numerous requirements for dry media blasting, resulting in significant cost increases. Implementation of Maximum Achievable Control Technology (MACT) will be required, such as effluent containment to meet the lower PELs. Water blasting and environmentally friendly chemicals do not generate airborne HAPs, nor does the xenon flashlamp/CO_2 process.

3. PLASTIC MEDIA BLASTING

Plastic media blasting (PMB) is a production ready process which is more environmentally friendly than chemical stripping and reduces operator exposure to health hazards. The process was approved by the Naval Air Systems Command for use on 0.016 inches and thicker aluminum airframes. The Navy issued a specification for "Plastic Media for Removal of Organic Coatings", MIL-P-85891. Of the six types of media described in the

specification, acrylic media is in use at the Depots and was used for the Navy's test program to determine safe operating parameters for paint removal from monolithic graphite/epoxy composite aircraft surfaces (5). The Naval Air Systems Command has authorized the use of PMB for paint stripping of composite laminate aircraft surfaces of 0.073 inches and greater in thickness at Depot level activities. PMB is well suited for aircraft paint stripping but generates significant amounts of hazardous waste and does not meet the environmental goal of minimizing hazardous waste in aircraft paint stripping.

4. NON-HAP CHEMICAL STRIPPERS

Early alternative candidates for methylene chloride based paint strippers included acid or alkaline-activated benzyl alcohol based removers and N-methyl pyrrolidone (NMP) based removers. Of the three, the alkaline-activated benzyl alcohol products have demonstrated the greatest potential for general use on naval aircraft. Acid-activated removers have limited application due to their corrosive effect on magnesium and the potential for embrittlement of high strength steel components, such as landing gear, tail hooks, fasteners, and wing attachment bolts. NMP paint removers are most effective at elevated temperatures (160 to 180°F), and, thus, more suitable to tank stripping operations.

In late 1992, the Naval Air Warfare Center Aircraft Division Materials Laboratory evaluated two benzyl alcohol based products, Turco 6776 (acid-activated) and Turco 6813 (alkaline-activated). Although Turco 6776 stripped laboratory panels in less than one hour, the product proved corrosive to magnesium and embrittling to high strength steel, as anticipated. In the laboratory tests, the Turco 6813 required approximately 24 hours, with 3 applications of stripper. However, field service evaluations of Turco 6813 conducted at Naval Aviation Depot Jacksonville (NADEP JAX) in April and December, 1993, on gloss painted P-3C aircraft demonstrated 90% coating removal within 9 hours and 98% coating removal within 4½ hours, respectively, with two applications of remover. Nine additional aircraft stripped in 1994 demonstrated similar results. Figure 2 illustrates one of the non-HAP chemical stripper demonstrations at NADEPJAX.

Since 1993, approvals for limited use have been granted for three non-HAP chemical strippers to five sites for seven platforms. A draft non-HAP paint remover specification (TT-R-2918) has been circulated for comments with an anticipated release date of February, 1997. Recent reports from NADEP JAX indicate greater difficulty in removing the coating systems from aircraft which have been repainted with self-priming topcoat (TT-P-2756) or with water-base epoxy primer (MIL-P-85582)/high solids urethane (MIL-C-85285). Additional testing will be conducted to identify more effective non-HAP removers for these coating systems.

In order to comply with the 1998 NESHAP deadline, non-HAP chemical strippers, intended for metallic surfaces only, must be considered as an interim process as well as a supplemental process to other emerging technologies. Based on such factors as cost, process efficiency, maintainability and suitability for aircraft skins, the most environmentally compliant stripping processes suitable for near term aircraft application involve medium pressure water technology and xenon flashlamp/CO_2 technology.
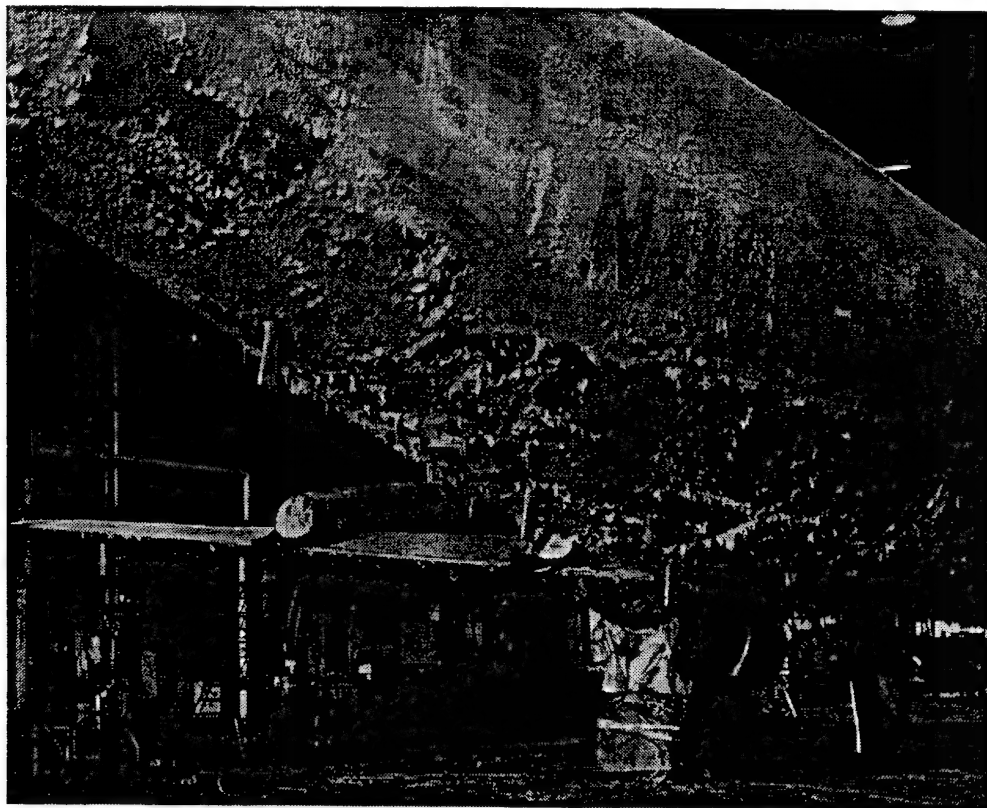
Figure 2. Non-HAP Chemical Stripper Demonstration

5. WATER TECHNOLOGIES

Warner Robins Air Logistics Center (WR-ALC) started investigating pressurized water paint removal methods in 1992 to replace methylene chloride used for stripping paint from the C-130 and C-141 aircraft at Robins AFB GA. The effort was targeted toward a modified Medium Pressure Water (MPW) process that uses 15,000 psi of water injected with sodium bicarbonate to enhance the effectiveness of the process. Since the implementation of this process in May, 1994, WR-ALC has documented an 87.7% reduction in the use of methylene chloride strippers. A materials properties evaluation was conducted to determine the effects of the modified MPW process on C-130 and C-141 aircraft substrates. Surface roughness, cladding erosion, fatigue life degradation, fatigue growth rate, shear strength of honeycomb core structures, peel strength, flatwise tensile and flexural strength were evaluated (6). WR-ALC determined that results were overall favorable and the modified MPW process began production prototype work on the C-130 in November, 1993.

Results of the modified MPW depainting prototype demonstrated that the majority of pre-blast masking or taping of critical components can be eliminated with proper blasting techniques and that rope caulking reduces ingress of blast media and prevents damage to polymeric sealants. However, the ergonomic properties of the process were less than desired.

To address ergonomic deficiencies, the current phase of the water technologies depainting effort focuses on improved equipment and application engineering. The goals of this phase are to industrialize and semi-automate the process while gathering all reliability and maintainability data on the new system. To increase process efficiency, a further investigation of the water paint stripping technologies has led to the selection of an Air Force qualified rotary nozzle currently used as part of the Large Aircrafts Robotics Paint Stripping system at Oklahoma City Air Logistics Center (OC-ALC). This system is a fully automatic process that utilizes 22,000 to 30,000 psi of water to remove coatings. Because the movement of the nozzle requires robotics, WR-ALC did not consider its use in the previous phases of the program. However, the current requirement to find the most ergonomic way to use water stripping leads to the use of an automated or semi-automated assisted device.

The semi-automated system concept uses three manipulator systems with six inch rotary nozzles that may lead to depainting the C-130 in 28 hours and the C-141 in 38 hours. This approach will allow 75-85% of aircraft stripping in the semi-automatic mode and is followed by handheld touch-up of the remaining portions with a newly designed handheld nozzle. A closed-loop approach to this process will filter paint and sealant particles and reuse process water. This system is scheduled for initial operation at WR-ALC during the fourth quarter of 1998.

6. THE XENON FLASHLAMP/CARBON DIOXIDE COATINGS REMOVAL PROCESS

The xenon flashlamp/CO_2 process evolved as a process improvement initiated during a 1990 Warner Robins Air Logistics Center (WR-ALC) attempt at coating removal using carbon dioxide blast. WR-ALC contracted McDonnell Douglas Corporation in April, 1991 to develop and demonstrate a concept using a synergistic approach, combining flashlamp technology with a low pressure CO_2 particle stream, to increase the depainting process rate and eliminate substrate damage. A process was developed, patented (7) and became known as the FLASHJET® process.

In February of 1992, the Navy joined the Air Force in testing the FLASHJET® process. During this year, WR-ALC sponsored a Producibility, Reliability, Availability and Maintainability (PRAM) to develop and demonstrate the viability of a 6-inch lamp prototype system to be installed on a robot for F-15 composite parts paint stripping. The program was completed with a successful stripping demonstration of a F-15 boron/epoxy vertical stabilizer.

The first high performance 12" system was fabricated in 1992. The USAF and McDonnell Douglas Commercial Aircraft Division conducted specimen stripping with the 12" system and testing was completed in 1993. Test results of the commercial specimen testing were submitted to the Federal Aviation Administration for review. Subsequently, the FAA and McDonnell Douglas approved the use of the xenon flashlamp/CO_2 process for paint removal on all McDonnell Douglas commercial aircraft.

A U.S. Navy Add-On Program (to the initial USAF contract) was completed in 1993 and a Follow-On Program was completed in 1996. The U.S. Navy programs provided a

materials properties test plan that incorporated Navy-specific materials and requirements testing. The programs centered on both metallic and composite materials testing.

6.1 Recent Developments The first fully capable production stripping system was completed in April 1996 at the McDonnell Douglas Helicopter Systems facility in Mesa, AZ. The stripping system is utilized on the AH-64A Apache aircraft pre-mod program and AH-64D Longbow Apache aircraft modification program. The stripping system is comprised of a 6-axis gantry robot system capable of stripping the Apache fuselage and various component parts including main/tail rotor blades, access doors, and other aluminum and Kevlar/epoxy parts. This production system is shown in Figure 3.

The most recent development for application of the process embraces the design integration of the Xenon Flashlamp/CO_2 system on a large mobile semi-robotic manipulator capable of positioning the stripping head over all moldline surfaces of large transport aircraft.

6.2 Technical Description This process, developed by McDonnell Douglas, utilizes a xenon flashlamp and carbon dioxide pellets. The system is comprised of the following subsystems: flashlamp, CO_2 pellet, effluent capture, process control and manipulator. A cross-sectional view of the flashlamp stripping head is depicted in Figure 4.
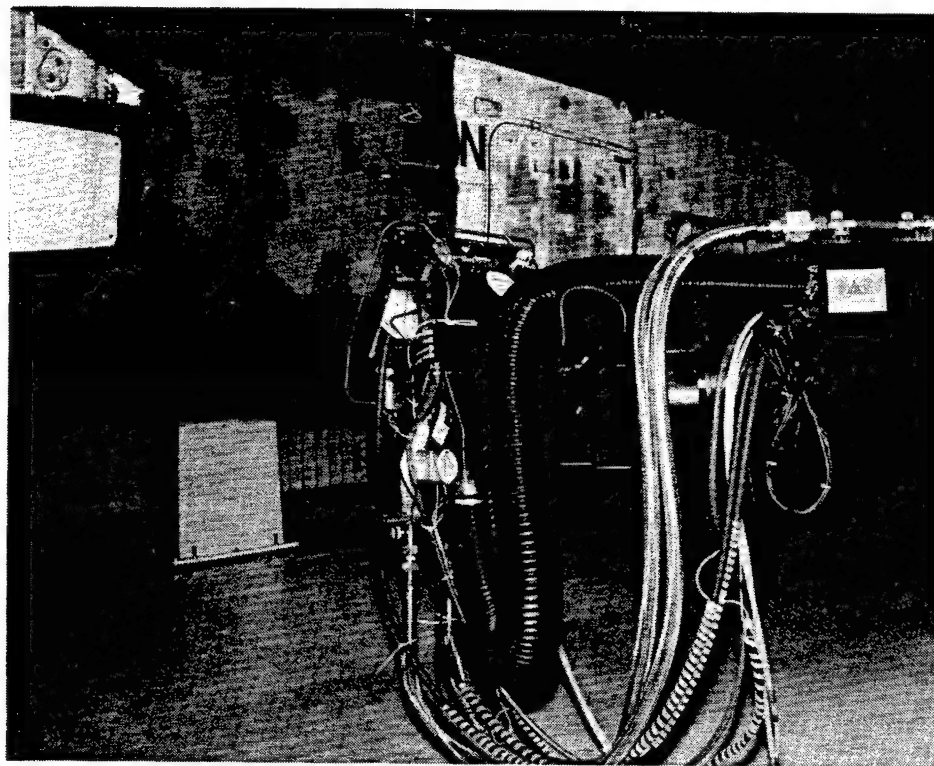
Figure 3. Xenon Flashlamp/CO_2 Production Stripping of an AH-64 Rotorcraft

The primary coating removal mechanism for the process is the irradiation of the coated surface with high intensity light that breaks the molecular bonds within the paint film,

reducing the surface coating to fine particles and gases. Low pressure carbon dioxide (dry ice) pellet blasting is used to sweep away the coatings residue and cool and clean the surface.
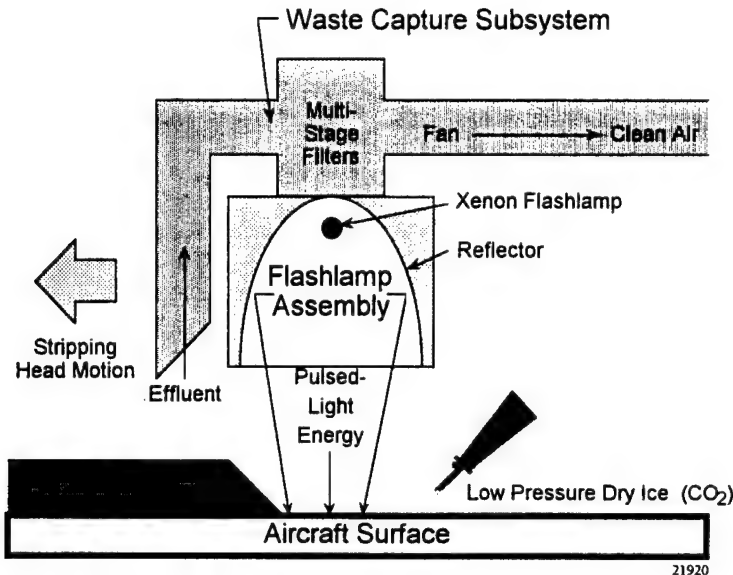
Figure 4. Xenon Flashlamp CO_2 Coatings Removal Process

The xenon flashlamp creates short pulses of intense, broad-band light that physically alters the paint and reduces it to a fine ash. The intense light is produced by discharging an electrical current into the flashlamp bulb that is filled with low-pressure xenon gas. The xenon gas absorbs the electrical energy and releases photons (light) that are emitted from the flashlamp head at wavelengths from the ultraviolet to infrared regions of the spectrum at a selected repetition rate (typically 3 to 4 flashes per second). The length of each pulse is approximately 500 microseconds, with an intensity dependent upon the input voltage selected. The heat produced by the light flashes increases the surface temperature by approximately 100°F (56°C), depending on the application and substrate. However, in most cases, the heat does not conduct through or damage most metal and composite substrates.

Removal rate and depth can also be controlled, either manually by varying the voltage input and pulse rate or automatically by using a color-sensing device. The xenon flashlamp/CO_2 process can selectively remove topcoats.

6.3 Benefits One advantage of using carbon dioxide pellet blasting in conjunction with the xenon flashlamp process is that the substrate and flashlamp head are cooled by the frozen carbon dioxide. This prevents possible structural damage of temperature sensitive surfaces that may occur due to the increase in temperature. In addition, carbon dioxide displaces the ambient atmosphere and acts as a shield on the substrate. This shield is actually a zone of reduced oxygen that prevents soils, fuels, and oils from igniting, thus eliminating the need for cleaning prior to coating removal.

Additional benefits include: low hazardous waste volume (no media), no media disposal costs, no media recycle requirements, no aircraft precleaning requirements, no adjacent component damage potential, no media intrusion potential, no post stripping clean up requirements, high aircraft throughput rate, favorable stripping rate, low aircraft damage potential, and minimal aircraft masking requirements.

The xenon flashlamp/CO_2 process can be used in a wide range of applications due to its versatility and ability to remove a variety of coatings without causing stress or damage to most substrates. This technology can be used to remove all paints and primers, including polyurethane and epoxy paints used in the aerospace industry. The process can be used to selectively remove paint systems down to paint primer or the substrate without damaging thin aluminum alloys, various carbon epoxy lay-ups, and butt joint gap sealants. Current plans for stripping non-metallic substrates will control the process to leave the primer coating intact.

Primarily because of reduced waste disposal and labor costs, the xenon flashlamp/CO_2 system provides a superior economic return on investment compared to the current process of chemical stripping or plastic media blasting for aircraft coatings removal. Studies have shown that the estimated operating (recurring) cost per square foot for aircraft coatings removal for the xenon flashlamp/CO_2 process is lower than the other processes considered. These costs can translate into impressive life cycle cost savings over a project life.

In summary, this process is a proven, environmentally compliant technology. It has been proven safe for all typical military and commercial aircraft substrates. It is a localized process, thereby reducing labor requirements. The process can perform selective stripping.

6.4 Testing The xenon flashlamp/CO_2 system has been extensively tested under the direction and supervision of the FAA, USAF and U.S. Navy. Mechanical properties tests have been performed on a variety of substrates representative of commercial and military aircraft structure. The testing captures the necessary materials properties data required by existing paint strip testing guidelines (8, 9).

A primary concern in choosing a paint stripping method is whether the chosen method will cause any damage to the underlying substrate or cause damage to the physical properties of the material. Under the USAF PRAM project, open-hole compression testing of boron/epoxy and fiberglass laminates was performed. The test results (10) revealed that neither composite material showed any signs of mechanical property degradation caused by the process when the specimens were selectively stripped of the topcoat and leaving the primer intact, which is the recommended method for stripping composites.

Additional testing conducted under a U.S. Navy Add-On Program (11) and a U.S. Navy Follow-On Program (12) indicated that the xenon flashlamp/CO_2 process can selectively remove paint systems down to paint primer or to the substrate without damaging impact on: 1) the mechanical properties of thin, structural aluminum alloys; 2) the mechanical properties of various carbon/epoxy layups; 3) adhesive bond strength; 4) butt joint gap sealant. In the Navy test program, paint was removed either to the primer or to the substrate, or stripped to a saturation condition by increasing the normal dwell time to remove paint to the substrate. The following paragraphs summarize the U.S. Navy test results:

Test results showed that the xenon flashlamp/CO_2 process is benign to aluminum alloy substrates. Maximum almen strip deflection was 0.5-mils using worst-case CO_2 parameters. Coating removal strip rates were optimized for four different paint systems and determined to be 2.0 to 4.0 ft²/min to the primer and 1.6 to 2.8 ft²/min to the substrate. Climbing drum peel testing of bonded aluminum skin-aluminum core sandwich assemblies and lap shear testing of bonded finger panels were utilized to evaluate the effects of removing paint on the adhesive bond strength of three different adhesive systems used by the U.S. Navy. Analysis of test specimens and results indicated that the xenon flashlamp/CO_2 process does not affect the adhesive bond strength of the specimens.

Spectrum metal fatigue life tests were conducted on A1 2024-T3 and A1 7075-T6 bare and clad material using open-hole and unnotched crack initiation specimens and crack growth specimens. Stripped specimens did not show a statistically significant difference from the pristine baseline material.

Composite testing under the U.S. Navy program was performed on carbon/epoxy specimens. Tests included tension and compression (open-hole and unnotched), fatigue, longitudinal flexure and interlaminar shear strength. No degradation was found in the material flexural, tension or compression strength, fatigue life, or material stiffness when stripping to the primer condition under normal operation. Additionally, no strength or stiffness degradation was caused in properly fabricated test specimens stripped to the saturation condition. Saturation was defined as additional 2/3 of the passes needed to strip to the substrate. Longitudinal flexure specimens were a surface sensitive lay up of [O_2+/-45, O, +/-45]. A few tests showed a 4% degradation of flexural strength properties when stripping to the saturation condition. Other tests showed potential increase or decrease in properties at the substrate condition, but not at the more severely stripped saturation condition. Since the xenon flashlamp/CO_2 system has the same basic effect on the epoxy resin of composite substrates, it is essential for process control not to dwell on areas with bare substrate exposed. Normal system operation includes color sensors which detect initial removal to the substrate and prevent excess dwell time.

Testing on MIL-S-8802 sealant was conducted, and despite evidence of pitting and some thickness loss, the butt gap sealant remained intact, adherent to the channel walls, and completely coating the underlying substrate. Repairs are easily effected by applying additional sealant directly over the sealant remaining in the gaps.

In summary, the testing performed to date on specimens stripped with the xenon flashlamp/CO_2 process indicates that the controlled process can be used on an indefinite number of paint/depaint cycles without deleterious effect to aircraft structure.

7. TECHNOLOGY TRANSITION

Current and emerging technologies suitable for paint stripping of aircraft without detrimentally affecting the structural integrity of aircraft metallic and composite skins were examined and compared. The selection of xenon flashlamp/CO_2 for further investigation and development as a process suitable for Navy aircraft provides the maximum reduction in hazardous waste generation. Transition of this technology to a full scale demonstration/validation of a system capable of safely depainting a large, cargo-size aircraft required a cooperative effort among the Navy at Naval Air Warfare Center Aircraft

Division, Patuxent River, Maryland; at the Naval Aviation Depot at Jacksonville, Florida; the Air Force at Warner Robins Air Logistics Center, Georgia; Mercer Engineering Research Center at Warner Robins, Georgia; and McDonnell Douglas Aerospace at St. Louis, Missouri.

A mobile, vehicle integrated manipulator is being integrated with a xenon flashlamp/CO_2 paint removal system to provide sufficient reach to demonstrate the process on a Navy P-3 type aircraft. The manipulator system is comprised of a heavy duty lift vehicle and platform mounted manipulator arms attached to the vehicle forks as shown in Figure 5. The vehicle has four axes of motion: boom lift, boom extension, platform tilt and platform swing, providing a maximum working height of 37 feet and a stable extension of 15 feet at ground level. Steering can be accomplished by two-wheel, four-wheel or crabbing (side to side) motion to facilitate positioning alongside an aircraft. The platform houses all components, including hydraulic and electric hardware, controllers and the operator. The manipulator arms are mounted on each side of the platform. Each of the arms can independently rotate in a vertical plane and extend and retract. The manipulator can access more than 180 square feet of an aircraft surface without relocation of the base vehicle.

The final phases of integration of the mobile manipulator-Flashjet® paint stripping system are scheduled for completion in 1997, leading to installation and demonstration/validation at Naval Aviation Depot, Jacksonville, Florida.
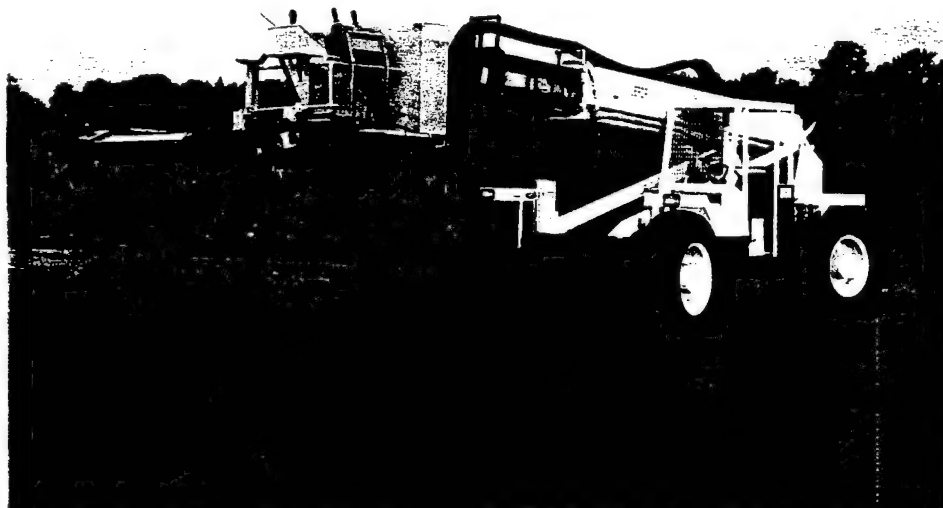

Figure 5. Manipulator Arm System Adapted to Heavy Lift Vehicle

8. CONCLUSIONS

Process studies, cost benefit analyses and materials testing have led to the conclusion that a multi-process approach provides optimum benefits in effecting environmentally safe and efficient stripping of the structural metallic and composite surfaces of military aircraft. Additional effort is required to demonstrate/validate the applications of the most promising emerging technologies to large (cargo size) and small (fighter size) aircraft.

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IMPLEMENTATION OF NEW COMPOSITE REPAIR MATERIALS TECHNOLOGIES ON U.S. NAVY AIRCRAFT

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ABSTRACT

In order to maintain a constant state of readiness, Navy and Marine aircraft structures must be repairable at land bases, aircraft carriers, and remote field locations. Since the first composite structure on navy aircraft was introduced in the early 1970's, the navy has been involved in many programs to develop composite repair methods. However, many repair materials, procedures, and support equipment were developed for each specific airframe and not standardized. Subsequently there is a cost burden for training fleet personnel to repair specific navy aircraft. The recent development of new repair materials and procedures has shown the potential for repairing highly loaded structures in the fleet and are adaptable to a variety of structures. Emerging navy aircraft embody larger percentages of composite structural weight along with new materials and more stringent performance requirements.

The Naval Aviation System Team (NAST) is evaluating the incorporation of new repair technologies to meet today's maintenance needs as well as those of future platforms. The NAST team members consist of Naval Air Systems Command (NAVAIR), Naval Air Warfare Center Aircraft Divisions (NAWCAD), and Naval Aviation Depots (NADEP). The status of the following repair programs will be presented: development of ambient storable repair materials, Navy stock system improvements for repair materials, support equipment for composite repair, bonded repair of metallic structures, high temperature repair materials, and rapid composite repair procedures.

KEYWORDS: Adhesives, Repair, Epoxy Resins

1. INTRODUCTION

Emerging aircraft such as the F/A-18 E/F Super Hornet, V-22 Osprey, and the two Navy versions of the Joint Strike Fighter (JSF) will contain 19-40% by weight of composite structures. These new structural materials come with a new set of requirements that may include operational temperatures ranging from 82 - 288°C (180 - 550°F), high cycle fatigue, thermal cycling, thermoset and thermoplastic materials, and post buckle composite structures. The Navy is involved in many development programs to meet these new requirements.

In order to sustain mission readiness, the Navy has a requirement to repair and maintain aircraft at carrier and field locations. Repairs must be performed in both peace time and battle conditions. At these locations, freezer storage is limited or non-existent. Only vacuum bag pressure and heat blankets are available to cure the repair materials. Support equipment must be portable and compatible with a variety of aircraft. The repairs in the battlefield must be performed rapidly using existing repair materials and restore structural integrity for a minimum of 100 hours of operation.

The Navy requirements for composite repair are too small of a market niche for many manufactures. Some of the needs are very expensive to produce and availability is extremely limited. Throughout the years, the Navy has successfully developed many new materials and common support equipment. However, vendors change their free enterprise marketing strategies and stop producing products for the Navy to pursue a more profitable market share. Similar problems have been experienced in manufacturing parts for future, current, and aging aircraft. Once a vendor stops supplying a product a new one has to be found and qualified with little promise of long term commitment to the needs of the Navy.

2. DISCUSSION

2.1 Development Of Ambient Storable Repair Materials   Previously, navy ambient storage conditions were defined in repair adhesive specification MIL-A-85705A as 12 months at 21-27°C (70-80°F) or 6 months 38°C (100°F). Various candidate repair materials were initially developed and tested under these ambient conditions. However, navy storage conditions were redefined as 2 weeks shipping/transition storage at 60°C (140°F) followed by 12 months storage at 38°C (100°F). Although many materials may meet the storability requirements of 6 months at 38°C (100°F), they may not withstand the increased exposure temperature of 60°C (140°F) in combination with the extended shelf life time of 12 months at 38°C (100°F). NAWCADPAX evaluated the effect of simulated shipping and ambient storage exposure conditions on Magnobond 6363, Hysol EA9390, and Hysol EA9394 [1]. The materials were tested for rheological, calorimetry, and mechanical characteristics.

2.1.1 Magnolia Plastics Magnobond 6363 Adhesive   This two part paste adhesive system is a formula modification of the Naval Air Warfare Center, Aircraft Division MIL-A-85705A developed system [2, 3]. The MIL-A-85705A specification requires that a repair adhesive be ambient storable at 21-27°C (70-80°F) for 12 months and at 38°C (100°F) for 6 months. Magnobond 6363 is formulated for ambient storability and has cure characteristics to prevent void formation during vacuum bag cure. This adhesive

will be qualified for structural bonded repairs on the V-22 Osprey aircraft utilizing a cure cycle of 93°C (200°F) for 2 hours. Magnobond 6363 is available in three packaging forms: quart kit cans, 50 gm bipacks sealed in vapor barrier pack with desiccant, and 2.5 fluid ounce semkits.

Testing has shown that Magnobond 6363 bipacks meet the Navy's shipping and ambient storage requirements for up to 6 months based on the physical and mechanical properties testing for cold temperature, room temperature and 82°C (180°F)/wet conditions. Field flow tests will be required to test Magnobond 6363 quart kit cans stored for more than 6 months to prevent adhesive with reduced mechanical properties from being used for aircraft repairs.

2.1.2 Dexter Hysol EA9390 Resin

This is a two part epoxy system for wet lay-up fabrication of composite patches. This impregnation resin will be qualified for structural repairs on the F/A-18 E/F Super Hornet, V-22 Osprey, and MH-53 aircraft. The resin is ideal for wet lay-up applications because it can be stored at ambient conditions, has low viscosity for impregnation, and has a long pot life. Studies have shown that the material can be stored at room temperature for up to 12 months [4, 5]. Double vacuum processing of this material has resulted in laminate qualities comparable to autoclave processed materials.

Although a previous NAWCADPAX study showed that Hysol EA9390 to be ambient storable according to MIL-A-85705A. The increase exposure temperature of 60°C (140°F) had a detrimental effect on the material properties. Testing has shown that special handling and storage conditions would have to be implemented for Hysol EA9390 bipacks since the Navy's shipping and ambient storage requirements cannot be met. The Hysol EA9390 bipacks will have to be shipped frozen and stored in freezers. According to a study by McDonnell Douglas, Hysol EA9390 quart kits can be shipped under navy ambient shipping conditions but must be stored in freezers.

2.1.3 Dexter Hysol EA9394 Adhesive

This thixotropic two part paste adhesive system can be used for potting, filling, and liquid shim applications. Hysol EA9394 adhesive will be used for the F/A-18 E/F Super Hornet and V-22 Osprey aircraft because it can be cured at either room or at elevated temperatures.

Testing has shown that Hysol EA9394 bipacks which can withstand the Navy's shipping environment. However, the Hysol EA9394 bipacks must be stored in freezers once the destination point has reached. According to a study by McDonnell Douglas, Hysol EA9394 quart kits can meet navy ambient shipping and storage conditions. However, after the storage of 12 months at 38°C (100°F), hardening of the part A resin on the top surface can occur which should be removed prior to use.

2.2 Navy Stock System Improvements For Repair Materials

Naval Air Systems Command tasked John Hopkins University / Applied Physics Lab to perform a Program Independent Analysis on the Navy stock system for composite repair materials. The findings of the Program Independent Analysis showed that the supply system was not responsive to current or projected needs for maintaining advance composite materials in the fleet environment. Current navy stocking procedures for composite materials results in large amounts of unusable material that is discarded as hazardous waste. Two part materials are treated as ambient storable materials regardless of the manufacture requirement for refrigerated or freezer storage. Perishable repair materials are shipped

and stored without temperature controls, shelf life is not maintained, and field quality control tests do not exist for many materials.

Under these shipping/storage conditions, unusable material can be supplied to the end user. Repair actions maybe delayed until acceptable material is resupplied. The material may be unusable for various reasons such as expired shelf life, hardening of the paste or film adhesives, improper storage/shipping conditions, or a combination of these situations. Some repair activities may request large quantities of repair materials in order to get a few usable units. The resulting hazardous waste is expensive to process and is expected to be more costly as emerging aircraft contain increasing amounts of composite structure.

To improve fleet readiness and to reduce logistical costs, the Advance Composite Repair Materials Process Action Team has been established between the Naval Inventory Control Point (NAVICP), Naval Air Warfare Center, Aircraft Division, Patuxent River (NAWCADPAX), Naval Air Systems Command (NAVAIR), and Naval Aviation Depot North Island (NADEP NI). The purpose of the team was to recommend solutions for improving the quality of repair materials being supplied to the fleet. The team's investigation focused on impact of material quality on fleet readiness, shipping/storage temperature controls, distribution time frames, storage conditions, and shelf life. The general findings are that material temperature controls vary throughout the distribution system, multiple agencies involved in material management resulting in process variation and complexity, and lack of information and training in handling perishable materials.

Some of the Advance Composite Repair Materials Process Action Team's recommendations include -18°C (0°F) shipping for all perishable repair materials, implement freezers at all stocking storage and transit points, set-up long term contract with vendors for direct delivery, increase prioritization for faster transportation times, and improved training for stock personnel and end users. The results that are sought from these recommendations are improved safe affordable readiness by preserving the mechanical properties of the repair materials, maintain weapon system readiness by improving material availability and logistic response time, and comply with mandates for reduced hazardous waste reduction.

2.3 Development of Support Equipment For Composite Repair In order to reduce inventory, maintenance, and training costs, the navy is investing and developing standard support equipment that can service a variety of aircraft. The equipment being used for composite repair is very critical with regards to quality control and providing reproducible results. Each aircraft has its own set of requirements and manufacturers will custom fabricate the additional support equipment at extra cost. Currently the navy uses tool kits to machine composites and temperature vacuum hot bonder controllers to cure materials. The Navy is investigating the development of a field portable double vacuum tool for processing Hysol EA9390 wet lay-up patches. Some of the candidate support equipment that the Navy plans to investigate are hot bonder controlled hot air guns for curing on complex shaped structures, rapid tooling equipment and materials for duplicating complex shaped parts, resin injection apparatus for repair of composite delaminations, portable automated C-scan inspection equipment, and computerized technical manuals.

2.3.1 Temperature Vacuum Hot Bonder Controllers The navy has several types of hot bonder controllers in its inventory manufactured by BriskHeat, Grumman,

McDonnell Douglas, and etc. The Navy developed and awarded a contractual specification for a common hot bonder. This system had the combined repair material cure requirements of several air platforms. Just when the Navy started to significantly benefit from this common support equipment, the vender changed its marketing strategy and did not renew the contract with the Navy for continuing purchases. However, technology and availability of hot bonder controllers in the commercial sector has improved dramatically with in the past few years. Each of the currently operational and emerging aircraft programs will have to search for the hot bonder controller that matches closest to their requirements. The Navy also can also open market competition for another common hot bonder controller.

2.3.2 *Composite Repair Tool Sets*   Composite machining is very specific to the types of structures being repaired. Likewise the tool sets sold by the aircraft manufacturers were very specific for the platform intended and could not be directly used on other platforms. The Navy did develop a common support tool kit that combined all of the aircraft requirements similar to the common temperature vacuum hot bonder controller unit. Unfortunately, production of the common tool set has been discontinued and the Navy will have to find a new vendor. Current operational programs will have to purchase the specialized tool kits from the aircraft manufacturer. Emerging aircraft programs will have to either piece together their own tool kits together or select one of the operational aircraft tool kits and provide a supplemental special kit for the new aircraft to reduce development cost.

2.3.3 *Field Portable Double Vacuum Tool*   Aircraft programs such as the F/A-18 E/F, V-22, and MH-53 will be soon qualifying Hysol EA9390 for processing wet lay-up repair patches. Details of the double vacuum process have been provided previously [4, 5]. Only a summary of the approach will be given here. The double vacuum debulk procedure requires the use of a rigid enclosure over a flexible vacuum bag. Vacuum is applied to the vacuum bag and rigid enclosure. Under these conditions, the laminate plies are exposed to a vacuum but no consolidation force is applied to the laminate. Heat may be used to reduce resin viscosity for more efficient air removal and/or staging of the resin. At a given point in the process, the vacuum in the rigid enclosure is vented which allows the bag to collapse onto the ply stack surface. Consolidation of the plies occurs under this vacuum pressure. Void free laminates with Hysol EA9390 resin result with good mechanical properties. Although the technical concept of the double vacuum tool shows promise, the Navy needs to investigate the best way to supply this as a common support equipment. The same problems that occurred for the common hot bonder and tool kits must be prevented from happening again.

2.4 Bonded Repair Of Metallic Structures   The traditional method of metallic structure repair used in the U.S. Naval Aviation fleet employs a combination of the following: stop-drilling cracks, riveting metallic patches over structural damage, replacing or remanufacturing damaged components and reskinning a section of aircraft. Each of these techniques has potential disadvantages. Stop-drilling can slow or stop crack growth, but is not a permanent repair in itself. Riveting metallic patches over structural damage is the most often used repair technique. However, both stop-drilling and riveting metallic patches can induce additional damage to underlying structure, may not eliminate crack growth, and may induce additional crack initiation sites from newly drilled fastener holes. While replacing damage parts with like-items can restore a part to its original configuration and load carrying capabilities, the process can be time consuming causing additional aircraft down time. Additionally, by replacing the part

with a like item, if the original cause of the damage is not corrected, the new part can be similarly damaged. Bonded repair of metallic structures offers numerous advantages over the standard bolted repair for metallic structures.

Various other organizations and government activities have completed numerous test and development programs with subsequent application to military and civilian aircraft. Some of these organizations include the Royal Australian Air Force, Defense Science and Technology Organization-Australia, Defense Research Agency-Farnborough Hants United Kingdom, British Aerospace Defense, Ltd., U.S. Air Force, Lockheed Aeronautical Systems Co., Warner Robins Air Logistics Center (WRALC), and the U.S. Air Force Academy (USAFA). These test and development programs highlighted the following advantages for composite repair of metallic structures: minimized patch thickness, tailorability of repair patch stiffness, minimized fretting, repair of complex curvatures, no damage induced to hidden structure, reduced strain in original part and potential economic savings over traditional bolted repairs. Numerous repairs with thousands of cumulative flight hours have been installed and monitored by these agencies. Repaired aircraft structures include C-141 weep holes in the wet wing skin integral stiffeners, F-111 wing pivot fitting, Mirage lower wing skins, C-130 wing planks and Boeing 767 keel beam. Repair of these structures typically use either Carbon/Epoxy or Boron/Epoxy composite repairs bonded on the aluminum structure. These repairs either repaired existing damage or were applied to prevent future fatigue damage. Studies also found the surface preparation process to be a critical step in having adequate bond durability. Durable bonding surfaces were achieved using grit blast, followed by silane treatment with subsequent application of an additional primer.

The U.S. Navy has ongoing technology work in composite repair of metallic structures. NADEP-Cherry Point and Naval Air Warfare Center-Aircraft Division(NAWC-AD) participate in a Wright Laboratory managed cooperative program between Boeing (Seattle), USAFA and the Royal Australian Air Force (RAAF), to share technology and service experience in the field of bonded repair. The goal is to have a technology overview document containing lessons learned, rules of thumb and a synopsis of the processes used. Material and Process, design, and nondestructive inspection volumes will accompany the overview document to give sufficient information to design, perform and monitor repairs.

There is a NAVAIR Technology team being assembled to address composite bonded repair of metallics technology development and implementation. This team consists of representatives from AIR-4.3, AIR-3.6.1, NAWC-AD 3.2, Lead Maintenance Technology Center and NADEPs. The NAVAIR team should help ensure acceptance by all navy and fleet engineering activities by ensuring a building block approach is used in the validation/verification process. This should allow all concerns and potential roadblocks to be addressed. There is also a proposed joint government initiative between the US Air Force and the Australian government to share technology information on composite repair of metallic structures.

As this technology matures, the opportunity for application is widespread. While newer aircraft have more usage of composites in the airframe structure, older aircraft use thin metallic skins as primary and secondary structure. These thin aluminum skins routinely crack and require repair. This is especially true with military and civilian aircraft aging and being flown longer. Even relatively new military aircraft programs

have parts prone to cracking. With continued development and testing, both military and commercial activities will begin relying more on this technology to keep their aircraft inventory flyable for longer service lives.

2.5 Development Of High Temperature Repair Materials   The trend in the aerospace community is an increased use of elevated temperature composites in the leading edges of supersonic aircraft and in structures surrounding the engine. Two classes of thermoset resins are often used in these applications. Typical bismaleimide (BMI) resins used in composite structures are exposed to temperatures of 204°C (400°F) in wet environments. High temperature polyimide resins such as PMR-15 and AFR700 are materials systems used on structures with operational temperatures of 288°C (550°F) which are beyond the capability of epoxies and bismaleimides.

2.5.1 Bismaleimide Prepreg Patch Repair Development   The first introduction of bismaleimide composites on naval aircraft necessitated the development of repair procedures for these components. The Naval Air Warfare Center has performed an evaluation on prepreg bismaleimide materials [6]. The goal was to develop patch materials which are storable at room temperature and which can be processed with field level equipment. The approach taken was to fabricate fully consolidated partially reacted, vitrified patch materials through a combination of advance staging and double vacuum processing procedures. Six bismaleimide composite materials that were evaluated were Hexcel F650/T-300, Hexcel F655/T-300, Ciba Geigy 5292/T-30, Ciba Geigy RX100-30/T-30, BASF 5250/G40, and BASF 5250-3/AS4. Processing procedures were developed for each of these systems and Room temperature storability was demonstrated. The Ciba Geigy 5292/T-300 prepreg was selected for fabricating a repair patch test article with the assistance of Naval Aviation Depot Cherry Point. Hysol EA9673 film adhesive was used to bond the patch on the test specimen. The repaired test article was exposed to a wet environment of 60°C (140°F) for 1 month prior to testing at 177°C (350°F). The test results showed promise for future development work.

2.5.2 Bismaleimide Wet Lay-Up Patch Repair Development   Emerging bismaleimide structures have complex shapes and highly curved surfaces which are difficult to repair using staged prepreg patches or bolt on metal plates. In order to repair complex structures, a wet lay-up patch is required. A wet lay-up patch will provide the capability to fabricate a highly conformable repair. The Naval Air Warfare Center performed an evaluation on a range of potential materials for elevated temperature repair [7]. This effort was directed at the development of patch materials which can be used for depot and field level repairs of 204°C (400°F) composite structures. Initial work has focused on bismaleimide (BMI) and other elevated temperature systems (dicyanate ester and high temperature epoxy). These materials were evaluated for vacuum bag processibility and mechanical properties. The conclusions that were drawn from this study are that processing concepts can be developed for the fabrication of wet lay-up formable patch materials for high temperature composites. The bismaleimide resins, Ciba Geigy Matrimid 5292 and BASF X206-44, were difficult to process during the wet lay-up procedure and lacked the required flexibility for the repair of complex shaped structures. The Hysol HyComp 400 epoxy resin had excellent processing and patch flexibility qualities, but the material requires refrigerated storage. Finally, the Ciba Geigy AroCy L-10 dicyanate ester composites shows promise as a wet lay-up patch material because of its flow characteristics and room temperature storability. Future studies will be based

upon optimizing the processing of the Ciba Geigy AroCy L-10 to improve laminate quality and mechanical strength.

2.5.3 *Further Development of AroCy L-10 For Bismaleimide Repair*

The Ciba Geigy AroCy L-10 resin was recommended for process optimization and evaluation of similar formulated resin systems [8. 9]. The materials supplied by Ciba Geigy include AroCy L-10, M-20, and M-50. The L-10 resin has a very low viscosity which leads to excessive flow during vacuum bag cure and results in resin dry laminates. M-20 and M-50 are solid resins that were mixed with the L-10 resin to create higher cure viscosities. A higher viscosity would be expected to reduce the resin leakage. However, the solid dicyanate esters did not improve cure rheology, laminate quality, and shear strength. Double vacuum procedures were developed to advance the low viscosity L-10 resin. Resin advancement resulted in highly formable wet lay-up patches and high quality vacuum cured laminates.

2.5.4 *Polyimide Repair Development*

Currently no depot or field level repair techniques exist for the repair of high temperature resin matrix composites. Existing repair materials cannot be applied due to the higher service temperature requirements and existing repair procedures and methods cannot be applied to PMR-15 due to the unique processing requirements of this material. The absence of repair materials would necessitate the removal, replacement and scrappage of damaged parts. The Naval Air Warfare Center has performed an evaluation of a range of potential materials for high temperature repair [10, 11]. This effort is directed at the development of patch materials which can be used for depot and field level repairs of 288°C (550°F) composite structures. Initial work has focused on polyimides (PMR-15, preimidized PMR, acetylene terminated PMR's and non methylene dianaline containing PMR's) and other high temperature materials (phenol triazine resin). Initial patch processing concepts have been developed for these materials. These materials were evaluated for vacuum bag processibility and mechanical properties.

The conclusions that were drawn from this study are that processing concepts can be developed for the fabrication of preconsolidated formable patch materials for high temperature composites. PMR-15 staged laminates can be produced, however, the material quality will be strongly dependent on the staging conditions used. The powder pre-pregged material form provided the best laminate properties from the processes studied. The acetylenic PMR material showed promise as a vacuum cure polyimide, but additional work is required for the development of suitable staging conditions. The phenol triazine resin composites were found to be easily processable, but the laminate properties were poor even after fiber surface treatments. Finally, the CPI-2310 pre-pregged composites shows promise as a stage patch material because of its flow characteristics processibility. With the incorporation of AFR700 composite structures on emerging aircraft, the Navy has teamed with the Air Force to develop repair concepts for a variety of structure types using this advance resin system.

2.6 Development Of Rapid Composite Repair Procedures

Composite repairs performed on naval aircraft during peace time must be capable of fully restoring the structural strength for the life of the aircraft. Often these repairs are time consuming due to the long heat cycles for the repair materials. In a battle field situation, these repairs must be performed rapidly to return the aircraft to "mission capable" within a few hours. Some repairs may not be required to fully restore the structural strength and need only last for 100 operational hours. Current qualified repair materials do not meet the needs of

rapid field repairs because they require freezer temperature shipment/storage and high temperature cure cycles.

To expedite these repairs, the Navy has investigated rapid heating methods and rapid curing materials. Some of the heating methods investigated were ultraviolet, ultrasonic, and induction heating. Ultraviolet radiation heating is not applicable for curing thick graphite composite patches. Ultrasonic heating was only applicable to small bonded joints. Induction heating showed the most promise to heat the material of interest: however, the susceptor in the adhesive bondline would cause adhesive disbonds. The rapid cure adhesives and composites that were investigated would require a lengthy qualification process prior to use on naval aircraft. The new heating methods and rapid curing materials would be a significant logistical constraint since they can only be used for battlefield conditions. The rapid heating methods require specialized equipment, calibration, and training. The cost of stocking, maintaining, and disposing of new materials to be used only in battle field conditions is significantly high. To maintain reduced logistics costs, rapid repair methods must be adaptable with current qualified repair materials and equipment.

Qualification of wet lay-up material, Hysol EA9390, for repairing composite structures in a remote field location is nearing completion on the F/A-18 E/F Super Hornet, V-22 Osprey, and MH-53 aircraft. Current wet lay-up repair procedures require 6 to 8 hours. Five hours of this repair time is used for double vacuum processing and vacuum bag curing. Developmental efforts at the Naval Air Warfare Center, Aircraft Division, Patuxent River, Maryland led to the evaluation of short double vacuum processing procedures and short cure cycle dwell times [12]. Hysol EA9390 impregnated IM7/5 harness fabric wet lay-up composite was tested to determine mechanical strength and thermal stability in a 82°C (180°F) wet environment for 100 hours of operation.

Magnolia Plastics Magnobond 6363 will be qualified for structural bonded repairs on the V-22 Osprey aircraft utilizing a cure cycle that takes over 3 hours to complete. An evaluation by Naval Air Warfare Center, Aircraft Division, Patuxent River, Maryland showed that cure cycles can be shorten by as much as 110 minutes and still meet thermal stability requirements for 100 hours with a hot wet operation temperature of 82°C (180°F) [13].

In a battle situation, the shorten cure cycles for Hysol EA9390 and Magnolia Plastics Magnobond 6363 provides the ability to complete repair actions and return the aircraft to immediate mission readiness. However, a documentation system must be established to inspect the patches after 100 hours of operation and to possibly post cured the materials for full material properties. Testing is recommended to develop design allowables and verify the effectiveness of a post cure for long term stability. Then the rapid repair patch would not have to be removed for a subsequent repair action if the material properties can be restored at a later time.

3. SUMMARY

The navy has been involved in many programs to develop state-of-the-art composite repair materials, processes, and support equipment. This type of development requires team work between Naval Air Systems Command (NAVAIR), Naval Air

Warfare Center Aircraft Divisions (NAWCAD), Naval Aviation Depots (NADEP), and Air Force. The repair programs meet many of the requirements of emerging, current, and aging navy aircraft.

Ambient storable materials do not meet the newly define navy storage conditions of 2 weeks shipping/transition storage at 60°C (140°F) followed by 12 months storage at 38°C (100°F). The increased exposure temperature of 60°C (140°F) had a detrimental effect on stored materials. To improve storage conditions and minimize hazardous waste, recommended changes are expected to be implemented in the Navy stock system. Standard common support equipment to be used with all current and emerging aircraft have strong costs benefits for reduced inventories and training. However, qualified vendors must be re-evaluated and new ones qualified on a regular basis to maintain availability. Several repair concepts have been developed for high temperature materials and are expected to be transitioned in to emerging aircraft programs. Shorten cure cycles for Hysol EA9390 and Magnolia Plastics Magnobond 6363 provides the ability to complete repair actions rapidly and return the aircraft to immediate mission readiness

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HEAT DAMAGE ASSESSMENT FOR ADVANCED COMPOSITES

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ABSTRACT

Technical issues, current approaches and recent progress at the Naval Air Warfare Center (NAWC) in investigating heat damage in advanced composites are discussed. Specific case histories of heat damage in naval aircraft show the effectiveness of current heat damage assessment techniques and also indicate needs for better, more accurate, non-destructive assessment methods. Ongoing efforts in characterization and assessment methods development include mechanical property testing, ultrasonic and thermographic non-destructive inspection (NDI), visual and micrographic inspection, thermal analysis, as well as efforts to analyze and understand chemical mechanisms of resin thermal degradation. Structural materials in both aircraft and tactical missiles see high temperature environments, and a better understanding of heat damage will be beneficial to both types of structures. Therefore, NAWC Aircraft Division and NAWC Weapons Division are coordinating efforts and resources to enable a more comprehensive investigation of the response of composites to heat. The ultimate Navy goal of this work is to detect and quantify heat damage and to understand heat-induced property changes in composite materials.

KEY WORDS: Heat Damage, Thermal Degradation, Epoxy

1. INTRODUCTION

Airframes and other structural components of both aircraft and missiles are exposed to extreme temperatures. Aircraft are exposed to fire, engine exhaust impingement, equipment overheat or repair malfunctions which can expose composite parts to temperatures sufficient to cause damage. The exterior surfaces of air-launched missiles, after launch, are rapidly heated to temperatures above the decomposition temperatures of most resins. In both aircraft and missiles, the properties of structural composites subjected to thermal damage environments need to be understood in order to intelligently utilize these materials.

This paper presents an overview of work ongoing at the Naval Air Warfare Center (NAWC) to investigate heat damage, identify the temperatures and time-at-temperature conditions (within the bounds of Navy heat damage scenarios) which result in an incipient damage region, develop new heat damage assessment methods, understand the chemical and physical mechanisms of thermal degradation and relate these to observed heat-induced property changes. In general, results to date point out the need for studying chemical reaction pathways, gas diffusion processes within composites, identifying specific damage mechanisms, and investigating relationships between property changes and underlying mechanisms. Ultimately, failure criteria that include a measurable heat damage state are needed for heat damage assessment and airframe design.

The high temperature behavior of composites first became of interest for the NAWC Aircraft Division (NAWCAD) in August of 1991, after a composite wing of an A-6 aircraft caught on fire. Questions arose regarding the flightworthiness of the aircraft and of the Navy's thermal damage assessment capabilities for composite materials. Five evaluation methods were initially studied: ultrasonics, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, thermal mechanical analysis (TMA), hardness and thermography (1). After two years the aircraft was certified and returned to service, but none of the non-destructive evaluation methods proved effective. This continuing need led to other programs either conducted or sponsored by NAWCAD. Techniques such as dielectric spectra, Raman spectroscopy, x-ray photoelectron spectroscopy (XPS) (2), Fourier Transform Infrared Spectroscopy (FTIR), and laser-pumped fluorescence (LPF) (3), were tried. Their results, when correlated to mechanical property losses, showed that none of these techniques could accurately define strength losses in a composite material using our current knowledge of heat damage. Ultrasonics, the standard depot level technique, is effective at identifying damage when delaminations are present, but studies show that there are heat damage scenarios where there is a loss in residual strength without crack formation or delaminations in the laminate (4). This effect, where there are strength reductions that are not detectable by current non-destructive inspection methods, is known as "incipient" heat damage. These case histories show the effectiveness as well as the limitations of current heat damage assessment techniques and the need for better, more accurate, non-destructive assessment methods.

Design of missile airframes in which there are extreme temperature gradients requires accurate material property data as a function of temperature, including thermal properties and degradation kinetics that govern heat transfer into a missile airframe. Graphite/epoxy composite structures can, in some cases, survive (with some damage) very brief exposures to temperatures in excess of the decomposition temperature of the epoxy (5). Heat transfer limitations can offer some protection during short time

exposures, especially if a porous char layer forms, or if blistering or delamination occurs, or if gas evolved from the outer surface carries away sufficient heat to protect the inner plies (6).

To better understand these observations and to investigate the mechanisms of heat damage, information on the chemical mechanisms and kinetics of degradation is needed. Thermal analysis and spectroscopy have been used to investigate decomposition of composites and matrix resins. Global degradation kinetics are typically measured by thermogravimetric analysis (7). Two TGA methods were used by the NAWC Weapons Division (NAWCWD) to measure weight loss kinetics of epoxy resins, an isothermal method and a dynamic, or constant heating rate, method. Results were compared to give confidence in predictions based on the kinetic parameters derived from TGA measurements. However, relying on TGA results to predict degradation rates has been criticized since TGA data does not give direct information on the true chemical kinetics of degradation reactions. Furthermore, mass transfer limitations or low volatility of degradation products can prevent weight loss, even when decomposition occurs (8,9).

TGA studies need to be supplemented by spectroscopic methods that can identify chemical changes and measure kinetics of the loss or appearance of identifiable chemical functional groups. Infrared spectroscopy has been used to examine the chemical changes accompanying thermal degradation in epoxies and other resins. In particular, Diffuse Reflectance Infrared Spectroscopy (DRIFTS) has been used to investigate heat damage in epoxy resins and composites (1,10,11). DRIFTS is used in this study to examine the chemical changes in powdered epoxy resins. Attenuated total reflectance (ATR) was used to measure chemical changes occurring at the surface of an epoxy disk.

Future work at NAWC will be directed towards providing the understanding necessary for more accurate prediction of time and temperature dependence of properties in high temperature environments, and will enable better airframe designs, better heat damage assessment methods, and more intelligent use of advanced composites. This will result in higher performance airframes, more lightweight structures, improved reliability, and reduced life cycle costs for naval aircraft and weapons.

2. MATERIALS

2.1 Neat Resin Neat resin samples were prepared by first degassing Fiberite 977-3 resin in a vacuum oven at 35°C (95°F). The resin was then cast in aluminum cake pans and oven cured at ambient pressure resulting in 2.54 mm (0.1in) thick panels. A convection oven was heated to 180°C (356°F) and the degassed resin was then placed in the oven, brought to temperature, and held for two hours. The ramp rate to temperature was approximately 5°C per minute. To prevent sudden exothermic reactions which were experienced by directly heating to 180°C (356°F), one hour temperature holds were incorporated into the cure cycle at 100°C (212°F), 120°C (248°F), and 140°C (284°F). The neat resin panels were subsequently cut into 7.62cm x 2.54cm x 0.25cm (3in x 1in x 0.1in) coupons.

Decomposition studies were conducted on neat diglycidyl ether of bis-phenol-A (Epon 828 from Shell), cured with meta-phenylenediamine, which was chosen as a "model" resin. Samples were cured at 80°C for 2 hours then at 150°C for 2 hours.

2.2 Composite Laminates   Composite laminates were made from Fiberite IM6/977-3 unidirectional prepreg material containing 64% fiber volume content. 16 ply unidirectional $[0]_{16}$ and quasi-isotropic $[0,+-45,90,90,+-45,0]_s$ laminates were hand laid-up using unidirectional prepreg and autoclave cured according to Fiberite specifications. After cure the laminates were cut into 7.62cm x 2.54cm x 0.25cm (3in x 1in x 0.1in) coupons.

3. EXPERIMENTAL

3.1 Environmental Conditioning   The samples were conditioned before thermal exposure to yield dry, ambient stored, and saturated coupons. Drying was performed in a convection oven at 38°C (100°F) and allowed to dry until no appreciable weight loss occurred. The ambient samples were stored in open air at ambient conditions. The saturated samples were held in boiling water according to ASTM D 570-81 testing procedure. Table 1 below shows the average weight loss or weight gain for the different sample groups.

Table 1. Weight gain or loss resulting from environmental conditioning.

Samples	Average Dry Weight Loss	Average Wet Weight Gain
977-3 Neat Resin	0.63%	4.18%
Unidirectional	0.29%	0.98%
Quasi-isotropic	0.32%	0.84%

3.2 Thermal Exposure   The conditioned specimens were thermally damaged in a high temperature furnace. The furnace was heated to a known temperature and coupons were then placed in the furnace. The coupons were subsequently removed after a period of either 5, 20, or 45 minutes. Furnace temperatures of 274°C (525°F), 302°C (575°F), and 329°C (625°F) were used. Upon removal from the furnace, the samples were air cooled to room temperature. Table 2 identifies the moisture condition of the specimens before heating and the temperature and time-at-temperature the coupons were exposed.

3.3 Ultrasonic Inspection   Ultrasonic testing was performed on a TechTrend International laboratory scanner using Arius II software. Scanning of the samples was performed using a 10 db gain level and a 5MHz concave transducer with a 5.08cm (2 in) focal length. Index and scan increments were 0.127cm (0.05 in) at a rate of 15.24 cm/s (6in/s).

3.4 Thermographic Inspection   Thermographic testing was performed on a Ambervu infrared imaging system located 46cm (18in) from the coupons. Inspection of the samples was performed using two flash heat lamps, each 2400 ws, located 61cm (24in) from the sample. Images were taken at 217 frames per second grabbing every seventh frame resulting in 200 frames.

3.5 Four Point Flexure Test   Flexural testing was performed according to ASTM standard D 790-86, "Flexural Properties of Unreinforced and Reinforced Plastics and Insulating Materials". Four-point

loading at one-third points. The support span was 4.1cm (1.6in) with a span-to-depth ratio of 16:1. The tests were conducted on an Instron test machine at a cross-head rate of 1.27mm/min (0.05in/min).

Table 2. Coupon level identification of exposure conditions.

Sample Set Coupon Label			Exposure Conditions		
977-3 Neat Resin	Unidirectional Laminates	Quasi-Isotropic Laminates	Temperature [°C]	Time [min]	Moisture Condition
9-525-05-S	U-525-05-S	Q-525-05-S	274	5	Saturated
9-525-20-S	U-525-20-S	Q-525-20-S	274	20	Saturated
9-525-45-S	U-525-45-S	Q-525-45-S	274	45	Saturated
9-576-05-S	U-576-05-S	Q-576-05-S	302	5	Saturated
9-576-20-S	U-576-20-S	Q-576-20-S	302	20	Saturated
9-576-45-S	U-576-45-S	Q-576-45-S	302	45	Saturated
9-623-05-S	U-623-05-S	Q-623-05-S	328	5	Saturated
9-623-20-S	U-623-20-S	Q-623-20-S	328	20	Saturated
9-623-45-S	U-623-45-S	Q-623-45-S	328	45	Saturated
9-525-05-D	U-525-05-D	Q-525-05-D	274	5	Dry
9-525-20-D	U-525-20-D	Q-525-20-D	274	20	Dry
9-525-45-D	U-525-45-D	Q-525-45-D	274	45	Dry
9-576-05-D	U-576-05-D	Q-576-05-D	302	5	Dry
9-576-20-D	U-576-20-D	Q-576-20-D	302	20	Dry
9-576-45-D	U-576-45-D	Q-576-45-D	302	45	Dry
9-623-05-D	U-623-05-D	Q-623-05-D	328	5	Dry
9-623-20-D	U-623-20-D	Q-623-20-D	328	20	Dry
9-623-45-D	U-623-45-D	Q-623-45-D	328	45	Dry
9-525-05-A	U-525-05-A	Q-525-05-A	274	5	Ambient
9-525-20-A	U-525-20-A	Q-525-20-A	274	20	Ambient
9-525-45-A	U-525-45-A	Q-525-45-A	274	45	Ambient
9-576-05-A	U-576-05-A	Q-576-05-A	302	5	Ambient
9-576-20-A	U-576-20-A	Q-576-20-A	302	20	Ambient
9-576-45-A	U-576-45-A	Q-576-45-A	302	45	Ambient
9-623-05-A	U-623-05-A	Q-623-05-A	328	5	Ambient
9-623-20-A	U-623-20-A	Q-623-20-A	328	20	Ambient
9-623-45-A	U-623-45-A	Q-623-45-A	328	45	Ambient

3.6 Thermogravimetric Analysis (TGA) Weight loss kinetics were measured by using a TA Instruments Model 2950 Thermogravimetric Analyzer on 3.8 - 4.0 mg resin samples in aluminum pans. Most resin samples were ground to a fine powder to prevent diffusion limitation of chemical reactions, but a few TGA runs were performed on bulk samples (disks approximately 8 mm in diameter and 0.5 mm thick) to examine the effects of diffusion limitation as occurs in real composites. Dynamic and isothermal TGA heating programs were

used to compare the two heating methods and obtain global kinetics and activation energies. Dynamic heating used heating rates of 2, 5, 10 and 20°C/min. from room temperature to 600°C. Isothermal heating used rapid heating (~100°C/min.) to the isothermal temperatures of 220, 235, 250, 275 and 300°C. Partially decomposed epoxy samples were prepared by isothermal TGA at different temperatures and quenching at specific times or weight loss.

3.7 Infrared Spectroscopy Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to obtain Fourier transform infrared (FTIR) spectra of the partially decomposed epoxy powder samples. Attenuated total reflectance (ATR) was used to obtain FTIR surface spectra of the partially decomposed bulk epoxy samples. All FTIR spectra were obtained with a Nicole 60SX spectrometer at 4 cm^{-1} resolution and an MCT-B liquid N$_2$ cooled detector.

4. RESULTS and DISCUSSION

4.1 Experimental Design   This study was designed to evaluate the detection of heat damage at low temperatures; temperatures at or below the onset temperature where delaminations begin to occur in a composite laminate, and at moderate exposure times of 5-45 minutes. Three sample sets were evaluated; one set of cured neat resin samples and two composite laminate configurations-unidirectional and quasi-isotropic. To provide a range of samples to test the effect of absorbed moisture, the samples were treated under dry, ambient and saturated environmental conditions. Table 2 identifies the various coupon configurations.

Three non-destructive methods were used to assess the degree of damage resulting from the above treatments: visual inspection, ultrasonic inspection, and thermographic inspection, and the combined results of these inspections were compared to the change in flexural strength of the materials. Typical damage modes observed are shown in Figures 1, 2 and 3. Note the striation marks in Figure 2 indicating stress build-up initiating in the middle of the resin and continuing to the surface.
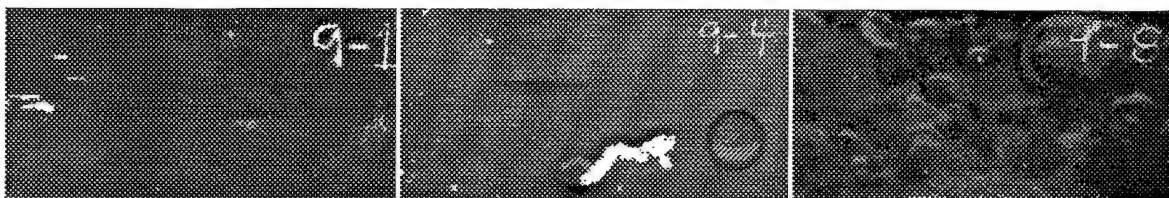

Figure 1. Saturated 977-3 Neat Resin Coupons 9-525-5-S, 9-576-5-S, and 9-623-5-S (from left to right) Showing Increasing Damage due to Increasing Thermal Exposure
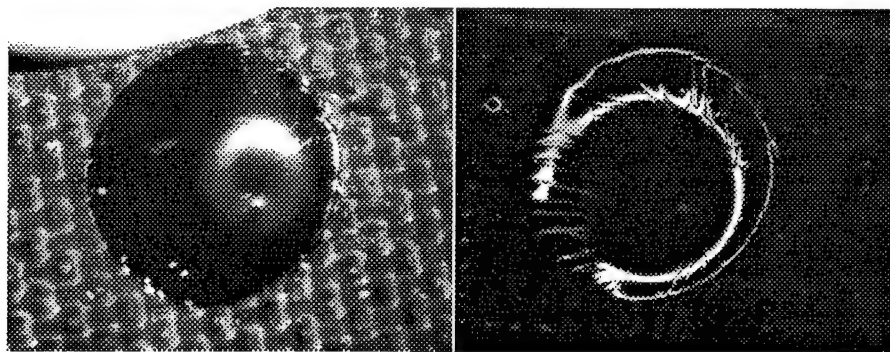

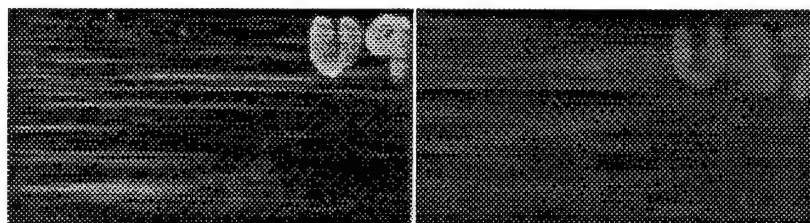Figure 2. Spalling due to Out-Gassing in 977-3 Heat Damaged Neat Resin

Figure 3. Ambient (left) and Saturated (right) Conditioned 977-3/IM6 Unidirectional Composites Exposed for 45 Minutes at 625°F

4.2 Visual Inspection   The neat resin lends itself well to visually evaluate the effects of the temperature treatments upon the polymer due to the cured materials semi-transparent nature. Figure 1

shows three of the coupons as they appeared after heating. These three are saturated coupons at 5 minute time exposures with increasing temperature exposure. It is seen that the amount of voids increase as temperatures increase. Using back lighting to aid the examination, observations of void formation delaminations after heating were noted and are documented in Table 3. The degree of damage was then qualitatively rated as either having no damage, some to moderate damage, or being completely damaged and are represented in Table 3 below. As the temperature and time-at-temperature increased, the degree of damage increased, but no visible damage was observed at the low temperature and short time-at-temperature exposures. Also noteworthy is that comparison of the ambient and dry conditions both yielded very similar observations, which stands to reason because they only differ slightly in their moisture content.

Table 3. Degree of damage rating for 977-3 Neat Resin visual inspection results.

4.3 Ultrasound and Thermography Inspection   Ultrasonic and thermographic scans were made on each of the specimens. Signal attenuation in the sonograms indicated damage from the heat treatments. The samples were then rated by roughly estimating the percent of the total area that exhibited defects. Samples with less than 25% inhomogeniety were classified as undamaged and greater than 25% were rated as damaged to some degree. Samples with deterioration so extensive that they could not be evaluated by these techniques were noted as totally damaged. This was done to distinguish intact 100% damaged samples from those that had entirely lost their structural integrity. The results of this scheme are shown in Figure 4.

Note according to this evaluation protocol, ultrasound inspection indicated no detectable damage at the lower temperatures and the lower time-at-temperature. Again, as in the case of the visual inspection results, the dry and ambient conditioned samples were comparable for the most part likely due to the fact that there is not an appreciable difference in their moisture content. It is also apparent that the higher degrees of damage were detected as temperature, time-at-temperature and moisture content increased.

The results of the thermography inspections are rated in the same fashion. The trends are the same as those found by ultrasound inspection; damage detection increases with temperature, time-at-temperature and moisture content. However, the results for the saturated samples for the unidirectional and quasi-isotropic materials yielded unusual results. The c-scan results show those sample groups to be extremely damaged although the thermography results show little damage for any of the coupons. Perhaps the extent of damage in these

Degree of Damage Detected by Ultrasonic C-Scan

	<25%	25% - 50%	50 -75%	75 - 100%	Total Damage

977-3 Neat Resin

Dry Conditioning	5 min	20 min	45 min
525°F			
575°F			
625°F			

Ambient Conditioning	5 min	20 min	45 min
525°F			
575°F			
625°F			

Saturated Conditioning	5 min	20 min	45 min
525°F			
575°F			
625°F			

Unidirectional

	5 min	20 min	45 min
525°F			
575°F			
625°F			

	5 min	20 min	45 min
525°F			
575°F			
625°F			

	5 min	20 min	45 min
525°F			
575°F			
625°F			

Quasi-Isotropic

	5 min	20 min	45 min
525°F			
575°F			
625°F			

	5 min	20 min	45 min
525°F			
575°F			
625°F			

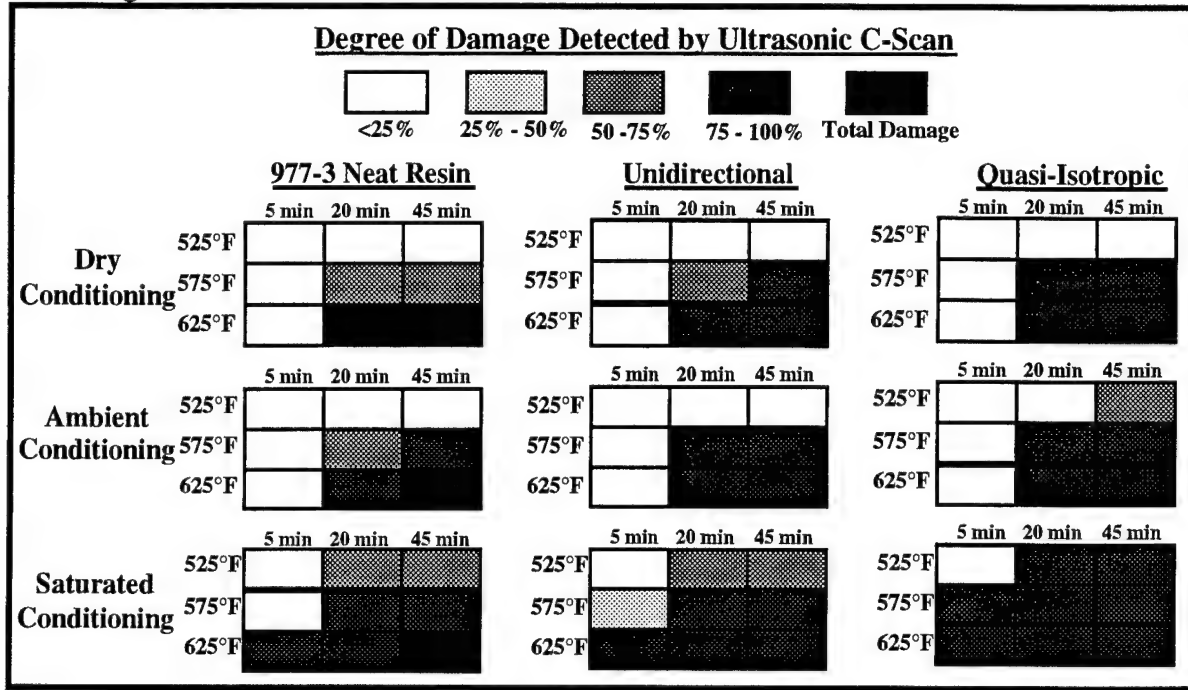|	5 min	20 min	45 min
525°F			
575°F			
625°F			

Figure 4. Degree of Damage Detected by Ultrasound

samples hindered penetration of heat and thus effected detection by thermography in the most severely damaged samples.

One significant draw-back to this type of rating is that it does not address the ratio of fine structure and multiple small areas of fine defects to large areas of inhomogeniety. This problem lends itself well to image analysis techniques that can be applied to evaluate relative sizes of damaged areas, and this analysis needs to be performed to gain greater insight into the interpretation of both the thermography and ultrasonic results.

4.4 Four Point Flex Test Resin properties are assumed to degrade faster than fiber properties under the influence of heat, therefore a flexure test was used to quantify the effect of heat damage on the mechanical properties of a composite. A comparison of the dry, ambient and wet exposed neat resins and the quasi-isotropic composite show a decrease in flexural strength with increasing time-at-temperature for the three temperatures. These results are shown in Figure 5.

Flexural strength decreased in most cases very significantly with increase in temperature, time-at-temperature and moisture content, which is very consistent with the damage detected by all of the above inspection techniques. Interesting to note, there is some loss in flexural strength at some of the exposures when the damage detected was either minimal or borderline at best, especially in the case of the dry and ambient conditioned samples. For example, the ambient conditioned neat resin flexural strength was

reduced to minimum values within 5-10 minutes exposed at 575-625°F, yet the amount of damage detected does not appear to indicate such a drastic change in sample homogeneity. In the case of the composite, low temperature exposure for 20 minutes again decreased the flexural strength, yet ultrasound results showed less than 25% damage.
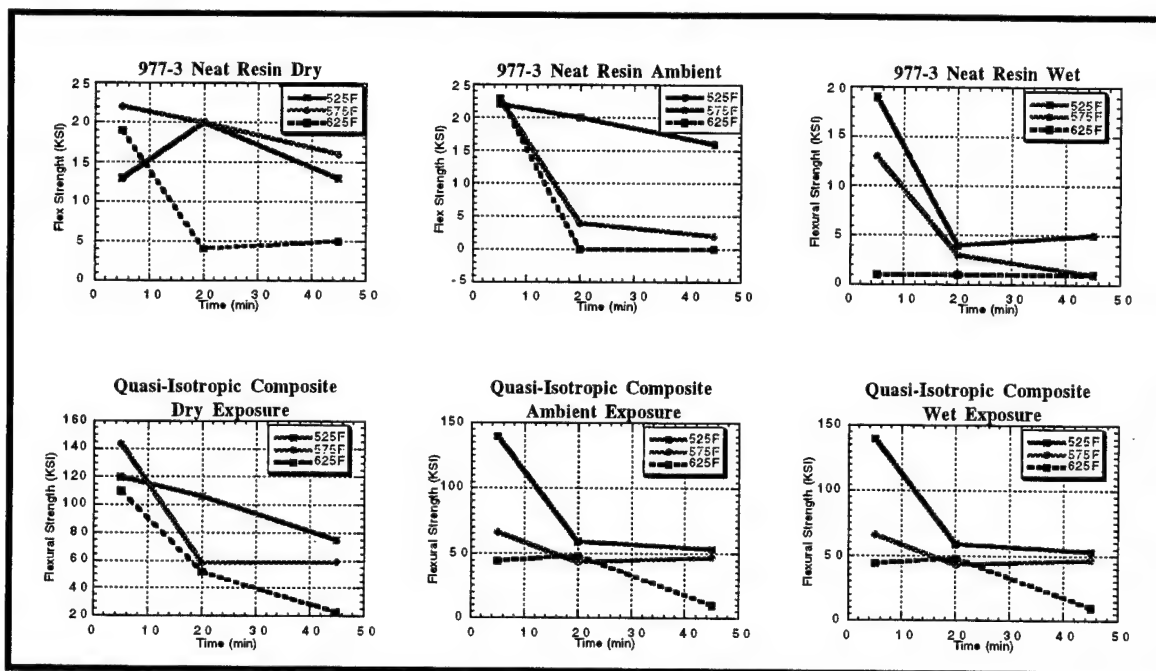

Figure 5. Change in Flexural Strength with Environmental Exposure and Heat Damage

Although the test matrix for this experimental design chosen for this study does not allow comprehensive analysis and correlation with the degree of damage detected by the above techniques, the results do illustrate some very definite trends when the decrease in flexural strength is compared to the inspection results.

4.5 Incipient Heat Damage   A very interesting feature about incipient heat damage in organic polymer resins is that the exposure time at different temperatures is not necessarily constant. In other words, although low temperatures are less likely to cause heat damage, when damage does occur at the longer exposure times, that damage is readily detectable. However, in the case of high temperature "flash" heating, the probability of detecting the damage decreases. At high temperatures and short times, exposure times are too short to allow gas pressure build up leading to voids and fissures, while at longer reaction times, even at low temperature, the onset of gas evolution and the accompanying formation of voids, fissures and blistering are readily detected by most any technique.

Realizing this description fits the case of the neat resin, however, the situation for polymer composites is different altogether. Incipient heat damage increases at lower temperatures and longer time-at-temperature, but is minimized at higher temperatures and shorter exposure times. This is shown schematically in Figure 6. "Flash" heating has immediate effect on matrix bond interface, possibly due to matrix bond interface fracture caused by the difference in the thermal expansion of the organic matrix and carbon fibers. Blistering and void formation and fiber matrix debond initiation is evident at longer time-at-temperatures, but other polymer matrix effects may not be detectable at shorter exposure times.

4.6 Activation energy by TGA The activation energy (E_a) for the thermal decomposition of the epoxy (Epon 828) was determined using both dynamic and isothermal heating for about the first 2 - 15 % weight loss over the temperature range of 220 - 300°C . Dynamic heating is the method normally used for composites and the activation energy is calculated as recommended in ASTM E 1641-94, "Standard Test Method for Decomposition Kinetics by Thermogravimetry". This method gives E_a =28 kcal/mole for the thermal decomposition of
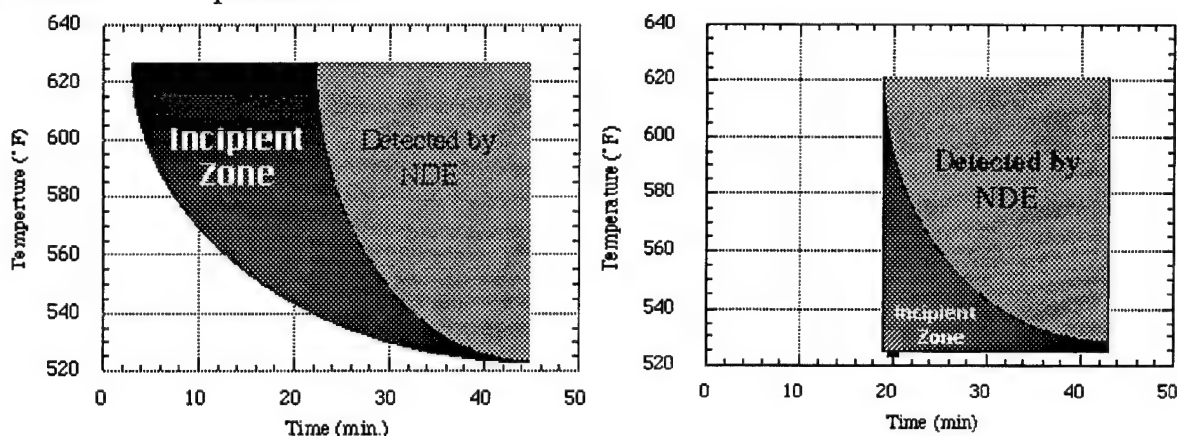
Figure 6. 977-3 Resin (left) and IM6/977-3 Composite (right) Incipient Heat Damage Zone

Epon 828 (220 - 300°C). This result is independent of global reaction order. The activation energy from the isothermal heating data is calculated using assumed first and second order global kinetics and the Arrhenius equation. Isothermal heating data for 220, 250 and 275°C show almost no difference between the first and second order rate constant fit. Therefore, this method can not distinguish between first and second order global kinetics. The isothermal activation energies determined from the rate constants and the Arrhenius equation are E_a=30 kcal/mole for first order and E_a=32 kcal/mole for second order (220 - 275°C). The dynamic and isothermal heating methods give similar activation energies for the thermal decomposition of Epon 828 over the 220 - 275°C temperature range.

4.7 Spectroscopy results Figure 7 shows DRIFTS spectra of partially decomposed powdered Epon 828 at 220°C in air from 0 - 17.4% weight loss (time = 0 - 240 min.). These spectra show the decrease or growth of specific functional groups within the epoxy and allow analysis of the chemistry of the thermal decomposition. Examination of the region around 1700 cm^{-1} in Figure 7 shows the growth of two carbonyl bands (C=O) due to oxidation of the epoxy. The carbonyl at 1730 cm^{-1} is from an ester, ketone and/or aldehyde and the 1675 cm^{-1} carbonyl is an amide. More detail on the changes in specific functional groups can be observed by plotting their referenced peak heights versus weight loss as shown in Figure 8. The 829 cm^{-1} para-aromatic -CH out-of-plane wag (functional group in the bisphenol-A portion of the epoxy) is constant and is used as the internal reference standard. Examination of Figure 8 and other DRIFTS data at 220°C show many interesting functional group changes for the initial 17% weight loss of the epoxy isothermal decomposition: (1) a linear growth of the 1730 cm^{-1} carbonyl; (2) an almost linear growth of the 1675 cm^{-1} amide carbonyl that starts to slow above ~12% weight loss; (3) an initial drop of the total aromatic (1509 cm^{-1}); (4) no change in the 2965 cm^{-1} -CH$_3$ (bisphenol-A); (5) a slight decrease in the -CH$_2$ at 2931 cm^{-1}; (6) rapid initial drop of the 695 cm^{-1} meta-aromatic (curative)followed by a leveling off; and (7) rapid drop of the remaining epoxide at 920 cm^{-1} (post-cure). Functional group decrease or growth is constant <u>versus weight loss</u> (i.e., independent of heating rate) over the 220 - 275°C
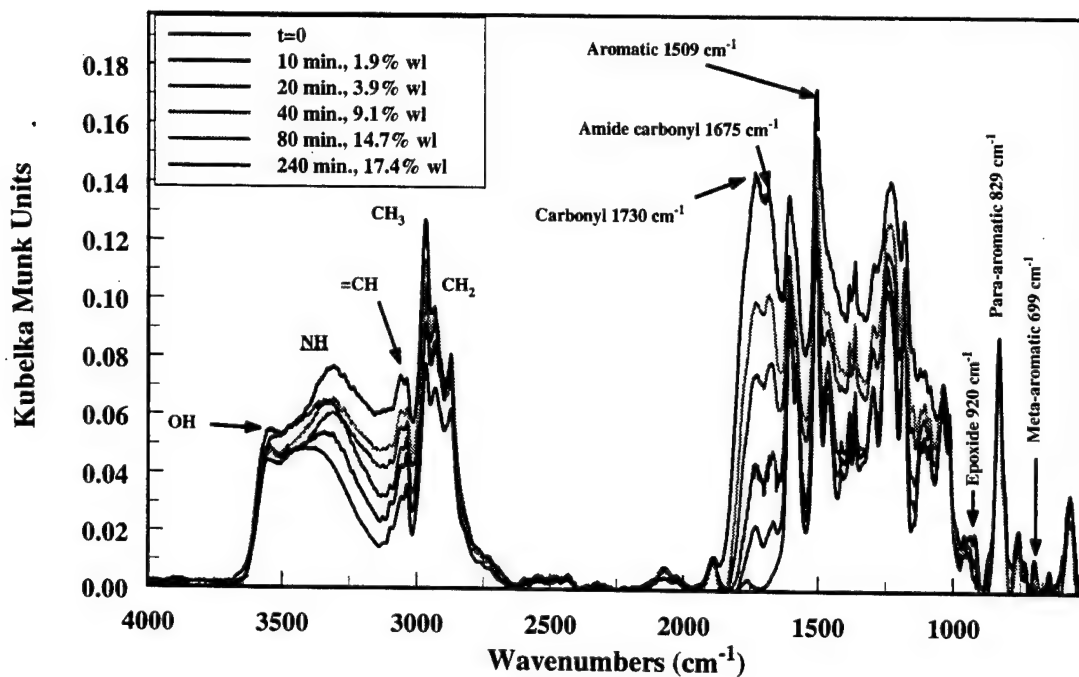
Figure 7. DRIFTS of Epon 828 Isothermal Decomposition at 220°C in Air
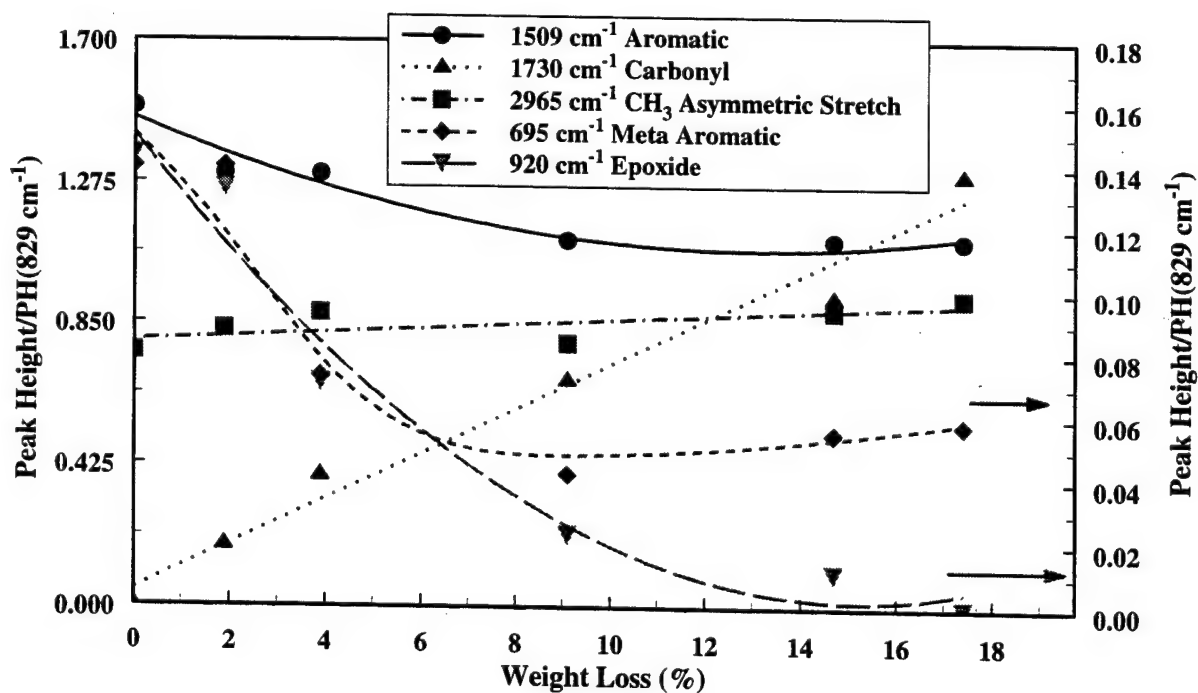

Figure 8. Referenced Peak Heights of Epon 828 Isothermal Decomposition at 220°C in Air

range. However, carbonyl growth or oxidation shows a slight "decrease" at 275°C (see Figure 9). The DRIFTS data indicates that the isothermal decomposition mechanism of Epon 828 is constant over the 220 - 275°C range. Other important observation from the DRIFTS data are that the bisphenol-A portion of the epoxy is stable up to 275°C, the curative linkage appears to be the weak link in the epoxy, post curing can be observed, and epoxy decomposition can be monitored with DRIFTS using either the 1730 or 1675 cm^{-1} carbonyl peak.

Kinetic information on specific functional groups can be determined using the DRIFTS data. Figure 10 shows the activation energy plot for the 756 cm^{-1} meta-aromatic peak calculated from first order rate constants (k1) at 220, 250 and 275°C. The E_a = 31 kcal/mole for the loss of meta-aromatic from DRIFTS data is in excellent agreement with the value of 30 kcal/mole from isothermal TGA data. A similar calculation for the growth of 1730 cm^{-1} carbonyl gives E_a = 27 kcal/mole using the DRIFTS data. This functional group specific activation energy data indicates that the loss of curative linkages may be the rate controlling step for the Epon 828 thermal decomposition.

Comparison of DRIFTS (powder) and ATR (disc) measurements of the Epon 828 thermal decomposition at 220°C show that the amide carbonyl growth <u>versus weight loss</u> is faster at the surface than in the bulk (see Figure 11). However, the TGA data shows that the powder gives a faster weight loss than the disc when plotted versus time. This data indicates that the Epon 828 thermal decomposition in air is initially a heterogeneous surface reaction.

5. CONCLUSIONS

Heat damage of 977-3/IM6 composites that result from moderate exposure times of 5-45 minutes over the temperature range of 274-328°C increases with the temperature, time-at-temperature and with moisture content. Damage that exhibited defects in the material, such as void formation, blistering, delamination and other changes in sample homogeneity could be readily detected by visual, ultrasound and thermography inspection. Of these three methods, ultrasound was the most comprehensive technique.

Comparison of the inspection results to resulting flexural strength of the material yielded a region of uncertain detectability by the above methods as to the extent the material had undergone degradation. The general boundaries for this region of incipient damage was proposed for the neat resin and the composite materials. The results suggest that damage of composites exposed to fire conditions is more likely to be detected by the conventional techniques than damage from longer times at low heat. Incipient heat damage is more of a concern when the materials are under dry and ambient conditions than in wet exposure conditions where heat damage in the presence of moisture was found to be readily detectable.

Next steps would be to further define the incipient heat damaged area, continue analysis of the thermography results, with particular attention to the fine structure observed in the thermographs and the heat dissipation rates, and to apply this experimental design to another polymer composite system.

Efforts are also being directed to identify chemical reactions that occur during heat damage and to quantify the degradation reaction kinetics. Diffuse reflectance infrared Fourier transform spectroscopy
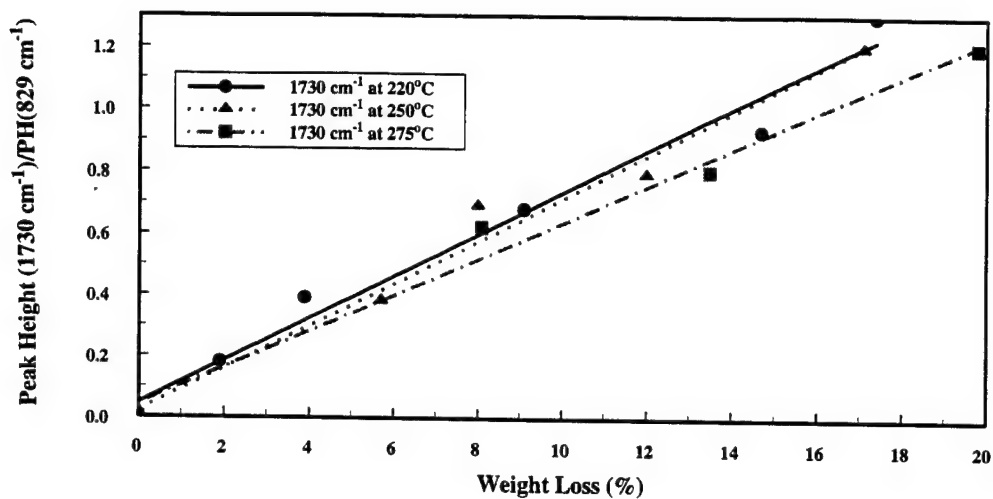
Figure 9. Epon 828 Thermal Decomposition for 1730 cm^{-1} Peak at 220, 250 and 275°C
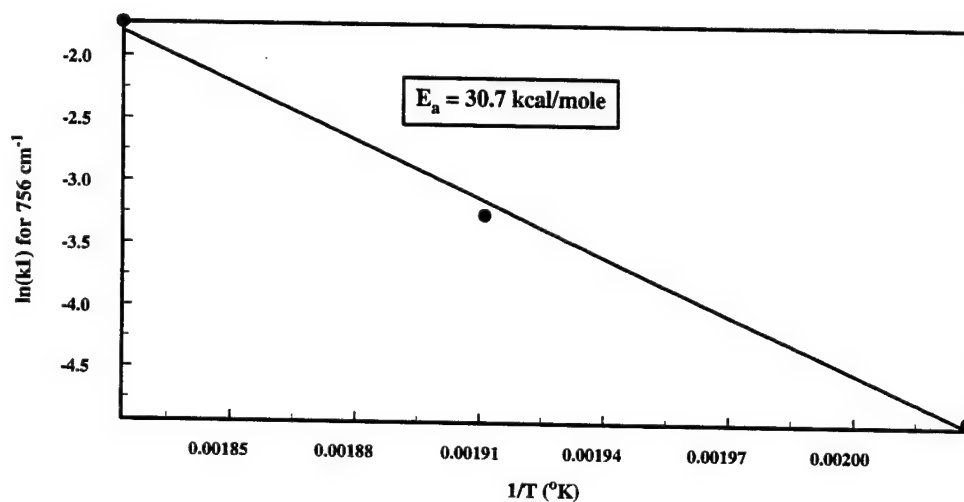

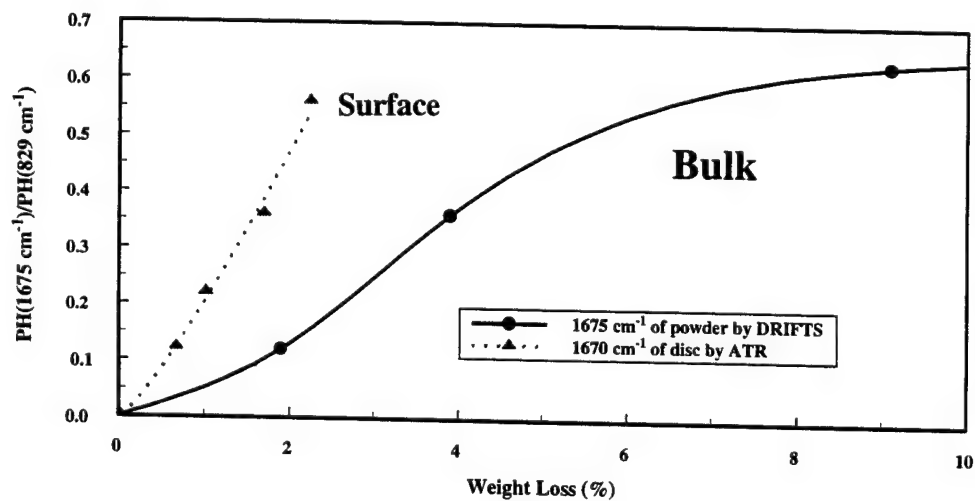Figure 10. Activation Energy From DRIFTS 756 cm^{-1} Meta-Aromatic Peak

Figure 11. DRIFTS of Powder Compared to ATR of Disc for 1675 cm^{-1} Amide Peak

(DRIFTS) and attenuated total reflectance (ATR) FTIR spectroscopy were used to measure chemical changes in epoxy resins after well controlled heat exposures. Combined with thermogravimetric analysis, the kinetics of weight loss can be related to the appearance and disappearance of specific functional groups or bonds that participate in degradation reactions. These results indicate the need for further analysis of decomposition species, especially in the gas phase. ATR measurements, compared with DRIFTS measurements show the importance of diffusion of gas species. Degradation reactions, such as oxidation, proceed much more slowly within solid resin specimens than at the surface.

6. ACKNOWLEDGMENTS

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THERMAL SPRAY COATING REMOVAL AT NAVAL AVIATION DEPOT JACKSONVILLE

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ABSTRACT

Thermal spray coatings are utilized extensively by aircraft engine manufacturers and at the Navy's overhaul and repair facility in Jacksonville, Florida. The removal of these coatings is frequently difficult and time consuming. Traditional removal methods are abusive. The acquisition of an ultra high pressure waterjet system for thermal spray coating removal has eliminated removal problems and improved productivity.

INTRODUCTION

The Naval Aviation Depot at Jacksonville is one of three Navy depots that repair, overhaul, and modify Navy aircraft. Principal programs are the P-3 ASW aircraft, F-14 fighter aircraft, EA-6B ECM aircraft, T-2 trainer aircraft, and GE F404, Pratt & Whitney J52, GE TF34, and Allison TF41 engines. A complete range of manufacturing processes is employed to provide everything from painting to electron beam welding.

Thermal spray coatings are used extensively by aircraft turbine engine manufacturers for clearance control, abrasive wear, wear resistance, and corrosion protection. Aircraft engine repair facilities make further use of thermal spray coatings for dimensional restoration/part salvage. Coatings that need to be removed at the Jacksonville depot include plasma spray, combustion spray, arc wire spray, and High Velocity Oxygen-Fuel (HVOF) in a wide variety of compositions.

COATING REMOVAL

The traditional techniques for removing thermal spray coatings can be generally characterized as abusive and time consuming. Mechanical removal methods include grit blasting, machining, and grinding. In all three cases, parent metal is lost and too many times the component is at maximum dimension or undersize after the operation. A good example is knife edge seals on rotating components in the GE engines. As the name implies, the seals taper to a knife-like edge which is easily damaged by grit blasting aggressive enough to remove a tenacious coating, such as plasma sprayed 95/5 nickel/aluminum. When single point machining or grinding to remove thermal spray coatings, it is often difficult to discern when the coating is completely removed. Consequently, the maximum dimension allowed may be where the removal effort stops, making future repairs difficult or impossible.

Chemical removal techniques can be expensive, tedious, hazardous, ineffective or all of the above. A typical removal cycle may involve several hours of soaking in a solution followed by mechanical removal of the remaining smut. Many commonly used coating materials are immune or resistant to chemical removal methods. Aluminum oxide (common on knife edge seals) is inert to nitric acid, which is the only chemical strip method available at Naval Aviation Depot Jacksonville (NADEP JACKSONVILLE). Components made of aluminum and steel are poor candidates for chemical strip because of their activity and sensitivity to acids.

There are many coatings that are difficult to remove because of their make-up. Bi-layered coatings may require two different techniques for removal, for example, grit blasting aluminum oxide off of knife edge seals and then soaking the exposed bond coat of 95/5 nickel aluminum in nitric acid solution. Some compositions are extremely resistant to chemical attack; bad actors at the depot are nickel/chrome/aluminum and aluminum oxide plus nickel/aluminum blends. Most carbide coatings must be ground

because they resist chemical attack and can not be single point machined. Very thick coatings can be especially troublesome.

A particularly annoying problem associated with thermal spray coating removal is thermal spray repairs done by the manufacturer on new parts. If the manufacturer mismachines a vane spindle pivot hole in a compressor case, and then repairs the defect with thermal spray coating and remachines, the repair is invisible to the buyer. However, when the case is immersed in a chemical bath to remove a coating elsewhere on the component, the factory repair is also removed and the compressor case is unusable.

WATERJET

Almost all of these problems are eliminated when using ultra high pressure water to remove thermal spray coatings. A typical ultra high pressure waterjet stripping cell consists of a six axis pedestal robot, an intensifier unit capable of generating 55,000 psi water, an enclosure with a turntable (and the robot), and some sophisticated software and nozzle technology. The Jacksonville depot uses a Pratt and Whitney unit referred to as Engine ARMS. ARMS translates to Automated Robotic Maintenance System. The Jacksonville system has been in operation for about a year and a half. Cost was $800,000. As of January 1997, 2,500 parts had been processed by the waterjet with no lost parts (one damaged and recovered) as compared with dozens using conventional removal methods.

There are two fantastic benefits to be gained using waterjet stripping technology for thermal spray coating removal: (1) the savings realized by not trashing any parts and (2) the reduction in turn around time from weeks to hours. A very conservative estimate on cost savings would be $1,000,000 in the first year of operation. "Hot parts" can be stripped of thermal spray coating same day, whereas the previous method may have involved three different operations in two different shops, and with the addition of some inevitable routing

delays in between shops, stretched the TAT to two weeks.

Additional benefits are legion. In some cases, process time is reduced over 90%. The waterjet can be used to remove overspray and selectively remove coatings without masking other coatings on the same part. Hazardous waste generation is reduced to only the coating material removed, reducing the need for nitric acid solutions and blast media. Estimated hazmat reductions at NADEP Jacksonville are 600 gallons of 50% nitric acid and 10,000 pounds of blast media per quarter. Out of round parts are a perennial problem when trying to machine coatings from a diameter--one side will clean up and the other will have coating remaining. This is an especially sticky problem when the diameter is at maximum and one side has not "cleaned up." Out of round is not an issue when using ultra high pressure water to remove thermal spray coating because there is no contact between the nozzle and the component; typical standoff distance is one to two inches. There is no limit on process cycles as there is when immersing some components in acid solutions. Thick coatings are no problem; thickness of brittle coatings does not affect the strip rate. And finally, "one size fits all." The same machine will remove almost any coating; there is no need for multiple machining centers or multiple solution tanks.

The coating removal mechanism of ultra high pressure water is a combination of fracture and erosion. Brittle plasma sprayed coatings such as aluminum oxide and tungsten carbide are readily removed. Tougher coatings may be more difficult to remove and a tough coating on a soft substrate, nickel aluminum coating on an aluminum substrate for example, may not work at all. High Velocity Oxygen Fuel sprayed coatings typically can not be removed, they are too tenacious and substrate damage occurs prior to complete coating removal.

Disadvantages in using an ultra high pressure waterjet stripper are few, but there is no free lunch. The enclosure and ancillary equipment require a fairly large amount of floor space and the footprint gets even larger if a water

reclamation system (to make the process water a closed loop) is used. The units are not cheap. Noise level can be borderline, approaching 85 dB. An ultrahigh pressure waterjet stripping system is complex and maintenance intensive. Successful operation requires personnel that will take a vested interest in the machine and assume ownership and responsibility.

In summary, the waterjet stripper can best be described as a huge increase in productivity. In the local colloquial, it's a moneymaker.

HVOF Sprayed Coatings for Navy Jet Engine Component Repair

Presented by:

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ABSTRACT

Continuing improvements to the mechanical properties of HVOF sprayed coatings has resulted in principal engine manufacturers utilizing this technology to implement new overhaul repairs for components. New techniques in powder manufacturing, new powder materials and new application techniques have made repairs possible for components that were either restricted to the limits of chrome or nickel plating or have been scrapped because no repair was feasible.
General Electric TF34, F404 and the Pratt and Whitney J52 aircraft engine components are being repaired with HVOF sprayed Tungsten Carbide, Tribaloy T-800 / T-400, and Inconel 625/718. Typical repairs involve bearing bores on main shafts, dimensional restorations and clearance control applications. Parameter optimization is performed by evaluating a taguchi matrix of variables such as gas ratio's, and spray distances to develop the best mechanical properties. Macro and micro hardness are evaluated in relation to tensile bond strength and microstructure. Optimized parameters are published in a repair document for use in the production shop during engine overhaul once all mechanical properties, grinding and finishing requirements are achieved. This paper will provide examples of three different coating qualifications accomplished at the Naval Aviation Depot Jacksonville.

Introduction

In 1993 the Naval Aviation Depot Jacksonville invested in a Metco Diamond Jet High Velocity Oxygen Fuel (HVOF) thermal spray gun and system to explore the possibility of qualifying to existing repair procedures developed by the principle engine manufacturers for overhauling critical components. In the DOD downsizing it was becoming a necessity to eliminate the reliance on contracting component repairs and for Depots to become more competitive on overhaul costs. This opened the door for exploring countless new applications for the HVOF system as the technology progressed. The depot has continually upgraded equipment to facilitate not only qualifying to existing repairs, but developing new repairs for parts that would have been scrapped for tolerance limitations, or plated with chrome or nickel. The latter repairs being increasingly more difficult due to tremendous pressure from OSHA and the EPA to reduce heavy metal carcinogens in the industrial environments. HVOF has become a viable technology to enhance repair capabilities and reduce the dependence on hazardous chemical processes for DOD repair facilities.

Tungsten Carbides

Traditionally applied as a plasma sprayed or proprietary D-Gun (Praxair, Union Carbide) coating, HVOF sprayed coatings of tungsten carbides are achieving far greater densities than plasma and similar or better mechanical properties than the D-Gun coatings. Extensive evaluations of manufacturing techniques for tungsten carbide powders with varying content of cobalt or nickel tougheners have led to a range of powders

for specific applications. Sintered, crushed and clad powders with 17% cobalt were chosen for the J52 oil system components because of the higher hardness values and improved wear characteristics associated with this powder. Lower cost and ease of application were also factors used in selecting this material. Material properties achieved were the following:

Microhardness	>HV1100
Bond Strength	> 12,000 psi
Density (Optical Image analysis)	<1% porosity
Bend	90° around 3/8" mandrel, No Cracks
Surface Roughness (Min.)	2-4 AA

Current applications include all oil system components on the J52 engine; driveshaft bearing surfaces, and gear shaft journals on helicopter gearbox components. This material is also a leading contender for several chrome and nickel plating application alternatives on the P-3 aircraft landing gear components because of the desirable properties.

Tribaloy T-800

Designed for aircraft engine components to sustain higher temperatures associated with gas turbines without degradation of mechanical or material properties, this coating also has excellent corrosion resistance along with intrinsic lubricity, provided by the molybdenum, for tremendous sliding contact wear performance. Current applications include the following F404 engine components: high pressure turbine rear shaft; fan drive shaft aft pilot diameter, and oil system bearing housings. Hardness values are in the Rockwell C40's depending on application parameters and bond strengths average 9500

psi. This coating has greater toughness than the carbide coatings but cannot achieve the same surface finishes and has lower densities with more prevalent unmelted particulate. Other disadvantages include difficulty dialing in the spray parameters to establish repeatability of coating properties. The coatings are also sensitive to substrate temperature during spraying and bond strengths are very dependent on surface preparation morphology. Coatings are limited to 0.25" thickness' because the residual tensile stresses associated with thicker coatings causes delamination and a reduction in the impact strength. These coatings are also viable alternatives for chrome and nickel replacement and are particularly suited for high temperature superalloys where corrosion is a concern.

Inconel 718 / 625

These coatings were designed to accommodate restoration of superalloys and provide excellent resistance to alkaline and acidic environments. Further component testing revealed that these components have superior performance in applications where the nickel aluminum coatings were used. Both have excellent high temperature properties and exhibit higher bond strengths than the tribaloy's averaging 10,000 - 11,000 psi. Hardness values range in the Rockwell 30's and 40's depending on gun, fuels and spray parameters. These coatings are also much easier to apply with HVOF in that propane. propylene, or hydrogen can be used as a fuel gas to facilitate use of any gun type. Also, once the parameter optimization has been performed the process is very repeatable and relatively insensitive to fluctuations in gas flows, pressures and powder feed rates. Coatings a very dense with relatively few unmelted particles and uniform oxide distribution. Finished coatings

resemble superalloys in that they can be milled, machined, tapped and drilled. Polished and honed surface finishes can be achieved in the 2AA range by grinding with sequential grit silicon carbide wheels. Current applications include F404 engine conical shafts; dimensional restoration on numerous internal shaft diameters; seals and snaps where nickel aluminum was previously sprayed and in repairs of exhaust frames and structural components that have been mismachined.

Conclusions

There are literally hundreds of thermal spray coatings commercially available and currently there are about 8-10 different thermal spray application methods to apply these coatings. HVOF spraying of the listed powders has provided an excellent combination of mechanical, material and chemical properties for aircraft and turbine engine overhaul and repair as well as the most promising potential for chrome and nickel plating alternatives. Lessons learned by the engineers in Jacksonville include the realization that there is not necessarily one specific coating that will work for all applications and that there will never be one alternative for either chrome or nickel plating. Only an all encompassing coating study, including parameter optimization, with component and coupon testing will provide enough data to determine feasibility for a specific application. The Naval Aviation Depot Jacksonville Materials Engineering Laboratory engineering staff continually investigates new coating and process applications for the facility and provides hands on shop support for the implementation of new repairs and new technologies. Currently the laboratory engineers are involved in three DOD funded programs that are investigating dual use

technology with HVOF as a potential for environmentally compliant coatings for the military and commercial sector.

ANALYSIS OF H-46 HELICOPTER ROTOR HEAD COMPONENT FATIGUE CRACKING

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ABSTRACT

From a materials engineering perspective, this paper is a summary of failure analyses performed on major rotor head components of the H-46 helicopter within the past several years. Failure modes, locations and causes are presented and discussed on a component by component basis. Fatigue was the dominant mode of crack propagation; however initiation of many failures was abetted by corrosion. Mitigation of failures via field inspections, repair process changes and a recent material substitution change from alloy steel to a precipitation hardening stainless steel is briefly addressed.

KEY WORDS: Corrosion, Failure Analysis, Fatigue

1. INTRODUCTION

The H-46 helicopter (hereinafter referred to as the H-46), also called the Sea Knight, is a tandem rotor helicopter powered by twin turbine engines. The H-46 was designed and manufactured by Boeing Helicopters. The H-46 has been in service with the U.S. Navy and Marine Corps for more than 30 years. During this lengthy service, the H-46 has undergone numerous upgrades and life extension programs as well as changing mission requirements. Currently for the Navy, it is primarily employed for both search and rescue (SAR) and vertical replenishment (VERTREP) missions at sea and ashore. For the Marine Corps, it is used primarily for missions involving transport of troops and supplies in operational maneuvers from sea. Secondarily, it is used for land-based SAR and miscellaneous test and evaluation functions. Currently there are more than three hundred H-46 helicopters in active service, approximately twenty-five percent with the Navy and the remainder with the Marine Corps. Maintenance responsibilities for the H-46 are divided among operating squadrons, intermediate field maintenance organizations and Naval Aviation Depots at Cherry Point, North Carolina and San Diego (North Island), California. Overall engineering and maintenance responsibility lies with the cognizant field activity at Cherry Point with significant input supplied contractually by Boeing Helicopters.

As mentioned previously, the H-46 has undergone numerous physical modifications in response to changing operational requirements and maintenance/repair needs over its service history, though none of those modifications would be deemed as major. The design of the tandem rotor heads and their major structural components, exclusive of blades, has remained essentially unchanged since inception. Some, but by no means all original components are still in service. Components are retired and replaced by new ones at the end of their designated service lives as determined via "safe life" design philosophy. Additionally, many components have been retired and replaced prior to reaching designated service lives because service related damage and degradation have rendered them unsuitable for continued service. When economically feasible and technically manageable, some damaged or degraded components are repaired and refurbished. These are then returned to service with appropriately assigned restrictions on usage, reduced life limits and requirements for periodic inspections. These restrictions and lowered life limits have been carefully derived from analyses and testing to verify viability and continued safe operation.

Despite all due diligence and care, some fatigue cracking of rotor head components has occurred. Such cracking has been attributable to the combined influences the harsh maritime operational environment and operating load characteristics arising from changed mission requirements. Only one of the instances of cracking reported herein involved catastrophic failure which resulted in a Class A mishap (loss of aircraft/loss of life). This was associated with failure of a pitch varying shaft which chronologically was the first case of pitch varying shaft cracking cited herein. The remainder of this paper is devoted to description of the major rotor head components, summary of fatigue cracking experienced over the past several years and to a brief discussion of a recent material change intended to increase resistance to fatigue and environmental degradation and, thereby, to avoid failures and reduce maintenance costs. The material for the major rotor head components, prior to the material change, has been AISI 4340 alloy steel per MIL-S-5000 (originally) and AMS 6415 (later), hardened to 1050-1200 MPa (150-170 KSI.) ultimate tensile strength (UTS). The new material, now phasing into service, is 13-8PH-Mo stainless steel per AMS 5629, aged to 1225-1375 Mpa (175-195 KSI.) UTS.

2. H-46 ROTOR HEAD COMPONENTS

Figure 1 is a photograph of an H-46 performing its VERTREP function. The tandem forward and aft rotor heads, each having three arms, are designated by arrows in the photograph. An important feature of the H-46 rotor heads which distinguish them from their commercial counterparts on the Boeing 107 helicopter is the capability for folding the blades of the former within the envelope of the body. This feature greatly facilitates parking and storage in confined areas. Figure 2 is a sketch depicting an H-46 with the blades of both rotor heads in the folded mode. The mechanistic provisions for folding complicate the configurations of both rotor heads and affect symmetry such that individual components are not necessarily interchangeable from arm to arm. Neither are individual components necessarily interchangeable from the forward to aft rotor head because the two rotate in opposite senses. Figure 3 is an exploded diagram of a "generic" rotor head arm minus the blade. This complex diagram is presented here not to give details of operation, but merely to identify the five major components and to indicate their relationship and orientation to each other. These major components are designated by arrows and letters on the diagram as follows:

TYPE A: Rotor Hub (RH) - This component (one per rotor head) connects centrally to the vertical drive shaft (not shown in diagram) protruding from the transmission. The three rotor head arms each connect to the RH and extend radially from it. See Figure 4 for further geometric detail of RH.

B: Connecting Link (CL) - This component (one per arm, three per rotor head) connects at its radially inner end to the RH via a horizontal pin joint which accommodates flapwise motion of the arm. See Figure 5 for further geometric detail of CL.

FIRST LINE OF TITLE HERE

C: Pitch Varying Shaft (PVS) - This component (one per arm) connects at its radially inner end to the radially outer end of the CL through a vertical pin joint which accommodates lead/lag arm motion. Additionally, it provides for changing of blade pitch by rotation about its horizontal axis along with the pitch varying housing (see D). See Figure 6 for further geometric detail of PVS.

D: Pitch Varying Housing (PVH) - As already indicated, this component (one per arm) in consort with the PVS (see C) provides for changing blade pitch. It is connected to the PVS internally via a tie bar which transmits axial and torsional loading between the two. See Figure 7 for further geometric detail of PVH.

E: Blade Attachment Fitting (BAF) - This component (one per arm) connects at its radially inner end to the radially outer end of the PVH via a vertical pin joint which is part of the blade folding mechanism. The rotor blade attaches to the radially outer end of the BAF through a pair of pin and clevis joints. See Figure 8 for further geometric detail of BAF.

3. FAILURE ANALYSES

3.1 Experimental Techniques Failure analysis techniques on all components included the following:

- Chemical analyses to determine material composition
- Hardness determinations to infer material heat treatment
- Visual and optically aided macroscopic observations to determine extent of cracking and fracture mode
- Scanning electron microscopic fractography to provide further evidence of fracture mode and details of failure initiation
- Metallographic examination to assess microstructure and effects of manufacturing/repair processes thereon

Additionally, in some instances, failure analyses included:

- X-ray residual stress measurements to assess propriety of manufacturing processes
- Replica transmission electron fractography to determine details of fracture propagation and duration
- X-ray micro-chemical analyses to determine active corroding species

3.2 Rotor Head Component Fatigue Cracking

3.2.1 Rotor Hub (RH) Figure 4 is a sketch of the RH with arrows and letters designating locations of fatigue cracking. Eighteen such cracks have occurred from 1969 to date. The number of cracks which have occurred at each location and the causes of initiation, if known or identified, are summarized in the following table.

Rotor Hub (RH) Cracking Summary

Location (See Fig. 4)	No. of Cracks	Cause of Cracking
A	6	Nicks/Gouges
A	2	Unknown
A	1	Corrosion Pitting
B	3	Unknown
B	2	Grinding Cracks
C	1	Corrosion Pitting
D	1	Nick
E	1	Grinding Crack
F	1	Forging Lap

Seven instances of RH fatigue cracking were caused by mechanical damage, nicks and gouges, attributable to tooling during repair operations. This issue was corrected by tooling modification and, as a result, no further fatigue cracking has occurred since 1989. There have also been four instances of fatigue cracking caused by manufacturing and repair processes (grinding cracks and forging lap). The issue of grinding cracks from repair processing was recently addressed and proper grinding procedures were established. There have been no further instances of fatigue cracking from grinding cracks since 1992. There also have been two instances of fatigue cracking from corrosion pits which occurred as a result of environmental degradation of Cd plating applied for corrosion protection. The most recent instance was in 1995. Because of the number of failures associated with the horizontal pin bores and because corrosion pitting has not been totally preventable, a recurring (based on flight hour intervals) eddy current field inspection has been instituted to find fatigue cracking and allow removal of cracked components from service.

3.2.2 Connecting Link (CL) Figure 5 is a sketch of the CL with arrows and letters designating locations of fatigue cracking. Seventeen fatigue cracks occurred in CL components between 1990 and 1993. The number of cracks at each location and attributed causes are summarized in the following table.

Connecting Link (CL) Cracking Summary

Location (See Figure 5)	No. of Cracks	Cause of Cracking
A	7	Ni plating > 0.25 mm thk.
A	1	Corrosion pitting
B	7	Ni plating > 0.25 mm thk.
B	2	Corrosion pitting

There have been fourteen instances of fatigue cracking attributable to a repair procedure involving buildup of the vertical pin bore via Ni plating. This buildup is necessary to return the bore to original dimensional tolerances after grinding to remove corrosion pitting. Additionally, three instances of fatigue crack initiation occurred from corrosion pitting in the bore absent of plating. Therefore, corrosion pitting is deemed to be the root cause of all CL cracking to date. There have been no instances of fatigue cracking since 1993. This is attributed to imposition of a 0.25 mm limit on plating thickness which restricts the associated fatigue strength debit from the plating process. On the downside, it also restricts the allowable amount of corrosion pit depth which can be remedied and the number of components which can be repaired. In view of the fact that corrosion pitting in the vertical pin bore has not been totally preventable, a recurring (based on flight hour intervals) eddy current field inspection was instituted to find fatigue cracking and allow removal of cracked components from service

3.2.3 Pitch Varying Shaft (PVS)

Figure 6 is a sketch of the PVS with arrows and letters designating locations of fatigue cracking. Seventeen fatigue cracks have occurred in PVS components from 1990 to 1995. The number of cracks at each location and causes are given in the following table.

Pitch Varying Shaft (PVS) Cracking Summary		
Location (See Fig. 6)	*No. of Cracks*	*Cause of Cracking*
A	11	Corrosion pitting
A	1	Plating arc burn
B	6	Wear

The twelve fatigue cracks in the vertical pin bore (location A) were all attributable to corrosion pitting as the root cause. The arc burn occurred in a repair procedure involving Cr plating necessitated by removal of corrosion pitting by grinding. The grinding and Cr plating repair have been supplanted more recently by installation of a sealed stainless steel liner in the bore after grinding to remove corrosion pitting. Material removal in both repair schemes was limited to 0.25 mm maximum. Because corrosion pitting of unlined bores has not been totally preventable, a recurring (based on flight hour intervals) ultrasonic field inspection was instituted to find fatigue cracking and allow removal of cracked components from service. The wear problem in the spider attachment lug (location B) has been addressed via a bushing installation change.

3.2.4 Pitch Varying Housing (PVH)

Figure 7 is a sketch of the PVH with an arrow designating location of circumferentially oriented fatigue cracks found in three components in 1991. All three cracks initiated from corrosion pitting on the exterior of the barrel. The pitting occurred where the edge of a metallic wire harness clamp caused a breach of the protective Cd plating. This problem was remedied by adding a rubber liner to the clamp. No further failures have been experienced. Because the potential for corrosion pitting remains, a recurring (based on flight hour intervals) ultrasonic field inspection has been instituted to find fatigue cracks and remove cracked components from service.

3.2.5 Blade Attachment Fitting (BAF)

Figure 8 is a sketch of the BAF with arrows designating locations of seventeen fatigue cracks found in blade attachment lug bores from 1991 to date. All seventeen cracks occurred in lug bores which had been ground to remove

corrosion pitting and Cr plated back to original size. Thus, corrosion pitting is deemed the root cause of failure. Deficiencies in the application of repair processes were associated with the first such fatigue failure. These included lack of shot peening prior to Cr plating, plating thickness beyond established limit (>0.25 mm), and slight overtempering of bore surface material during grinding. Each of these deficiencies was addressed and appropriately corrected; however, failures continued to occur in components absent of repair deficiencies. Because of this, a recurring (based on flight hour intervals) ultrasonic field inspection was instituted to find fatigue cracks and allow removal of cracked components from service. A new repair procedure involving grinding and installing sealed liners in corroded lug bores was instituted because the BAF cracking problem persisted. Unfortunately, the most recent BAF failure was in a lug bore with the liner repair. There was a deficiency in shot peening technique which has now been corrected.

3.3 Material Substitution As may be inferred from the preceding discussions, the root cause of most of the component failures is attributed to corrosion pitting either directly as a source for fatigue crack initiation or indirectly whereby repairs to components necessitated by removal of corrosion pitting have had a role in abetting fatigue failure. In many more instances, the occurrence of corrosion pitting, after breakdown of corrosion protection, e.g., Cd plating and paint systems, has been of such severity as to render components unrepairable and unsuitable for further service. Indeed, a recent study (1) has concluded that the annual cost of corrosion to the H-46 program exceeds $130M. Though representing more than just the costs associated with rotor head components, this estimate is deemed conservative since it appears not to include costs of replacing unrepairable corroded components.

A Dynamic Component Upgrade (DCU) program was initiated approximately three years ago as a collaborative effort among U.S. Navy and Boeing Helicopters engineering and logistics personnel. The DCU program was motivated by the economics of corrosion costs and, even more importantly, by implications of corrosion and fatigue cracking on flight safety. One of the chief thrusts of the DCU program involved a material substitution for the five major rotor head components which are the subject of this paper. The new material selected to replace the AISI 4340 alloy steel (1050-1200 Mpa UTS) is 13-8PH-Mo precipitation hardening stainless steel (1225-1375 MPa UTS). The principal benefits sought and expected from the new material were greatly increased resistance to atmospheric pitting corrosion and improved fatigue strength. Fatigue strength increases have been verified via extensive fatigue testing of coupons and components (2). Increased corrosion resistance likewise has been verified via salt fog chamber testing of coupons and components. Further, slow strain rate coupon tests have demonstrated non-susceptibility of the new material to stress corrosion cracking (2).

Minor geometric changes in components have also been accomplished without re-tooling or extensive manufacturing process changes. Avoidance of potential problems associated with galling and crevice corrosion of the new material has been addressed. Success is being assessed in an ongoing surveillance phase of the DCU program. At present, about forty H-46 helicopters are equipped with DCU rotor heads. The fleet leader has accumulated 400 hours flight time. Phase-in of DCU rotor heads will be completed by the year 2000.

4. SUMMARY AND CONCLUSIONS

A summary of fatigue cracking failures by component with predominant locations and root causes is presented in the following table.

Summary of Fatigue Cracking

Component	No. Cracked	Predominant Location	Predominant Root Cause(s)
Rotor Hub	18	Horiz. pin bore	Nicks/gouges/ grinding cracks
Connecting Link	17	Vertical pin bore	Corrosion pitting
Pitch Varying Shaft	18	Vertical pin bore	Corrosion pitting
Pitch Varying Housing	3	Barrel	Corrosion Pitting
Blade Attach. Fitting	17	Blade attach. lugs	Corrosion Pitting

The underlying root cause of most fatigue cracking in H-46 rotor head components has been corrosion pitting. This has been remedially addressed through a material change now being phased into service. Components of the older material, which have exhibited susceptibility to pitting and fatigue cracking, are subject to recurring non-destructive field inspections. Other causes of fatigue cracking, e.g., nicks, gouges and grinding cracks are now being avoided by changes in component manufacturing and repair processes.

5. References

1. H. Mindlin et al., DoD Metals Information Analysis Center (MIAC) Report 8, February 1996.
2. Boeing Helicopters, unpublished data.
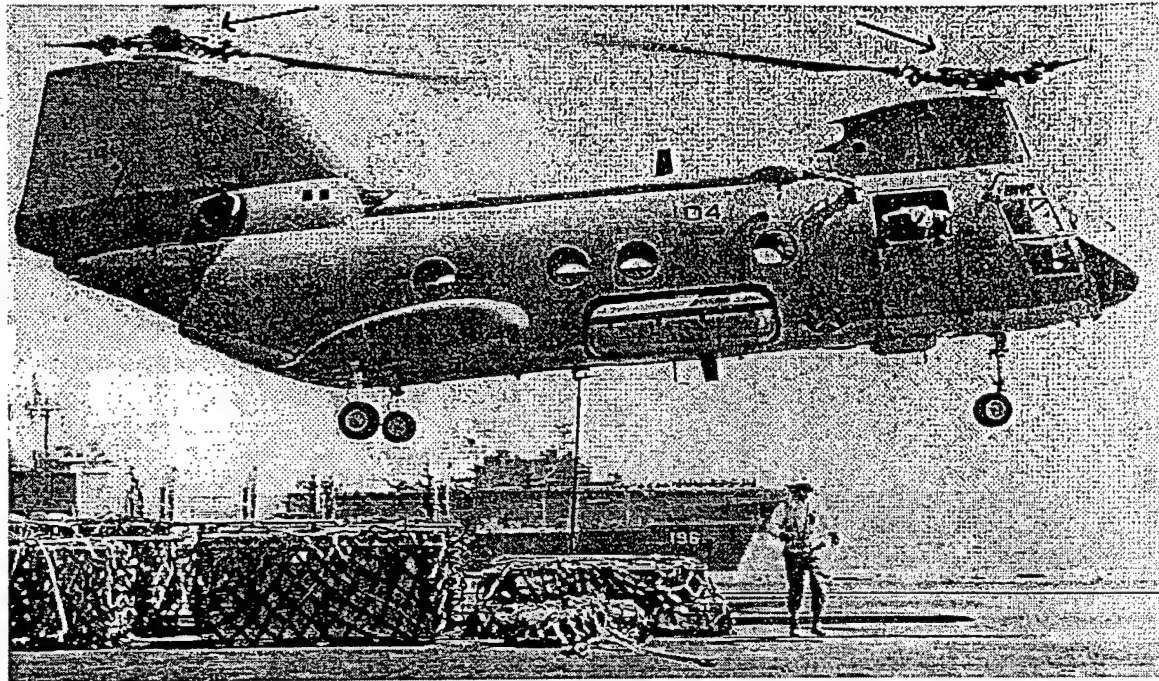
6. Acknowledgments

Figure 1 Photograph of H-46 Helicopter Performing VERTREP Mission
Photograph Courtesy of Boeing Helicopter

14 m (46 ft.)
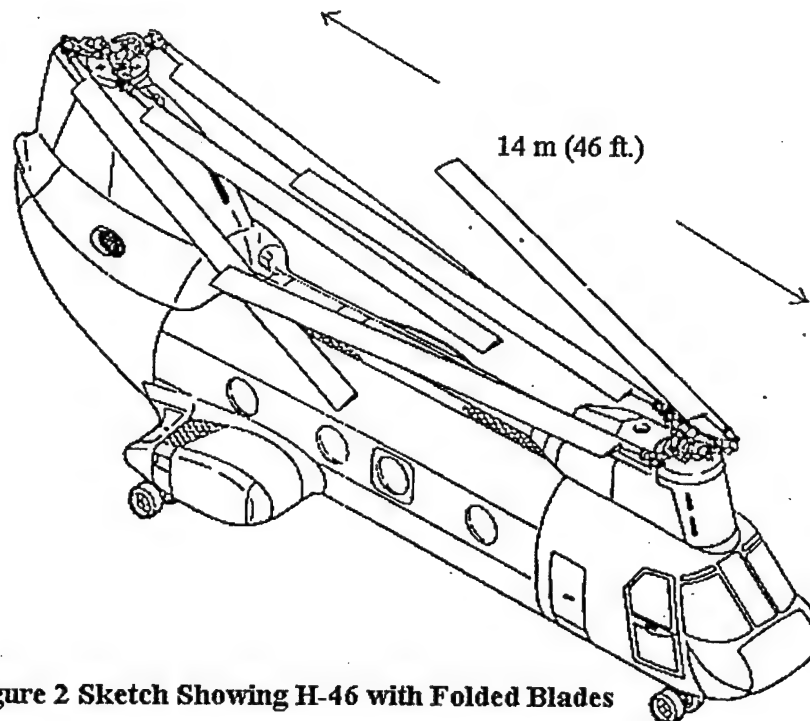
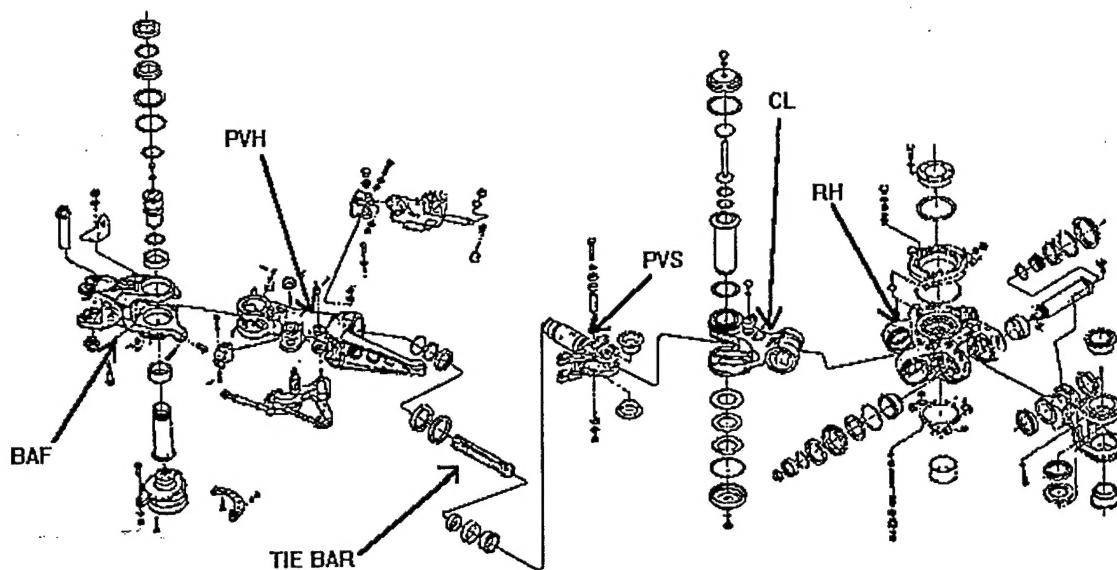**Figure 2 Sketch Showing H-46 with Folded Blades**

Figure 3 "Exploded" Sketch of H-46 Rotor Arm
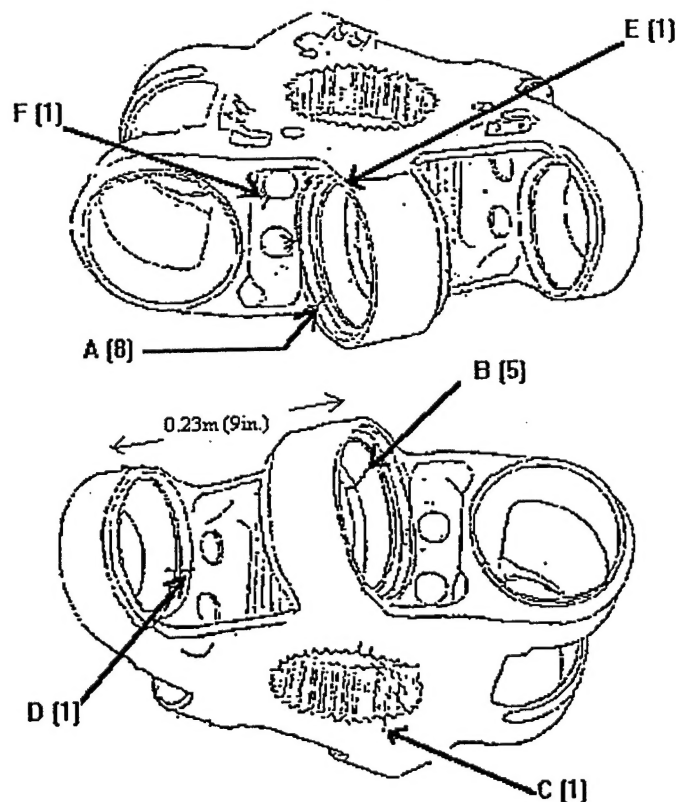Letters and arrows designate major components.

Figure 4. Rotor Hub (RH) Geometry and Crack Locations
Arrows and letters (A- E) designate crack locations.
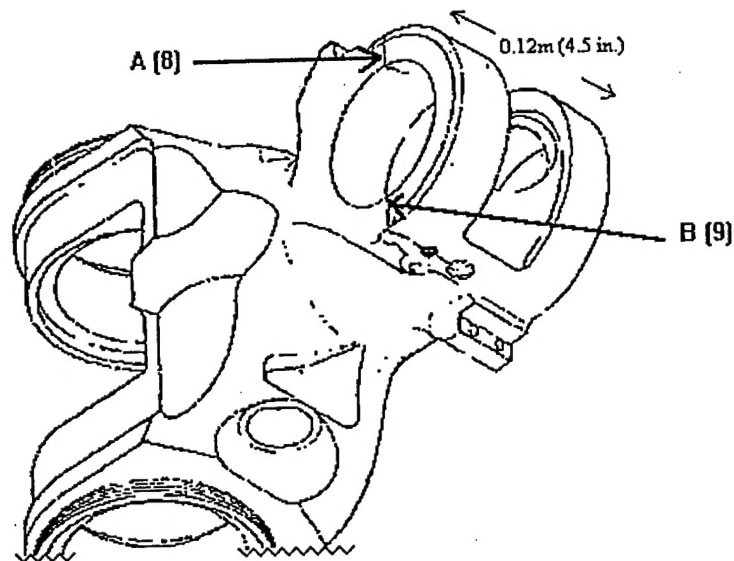Numbers in parentheses indicate number of cracked components.

Figure 5 Connecting Link (CL) Geometry and Crack Locations
Arrows and letters (A & B) designate crack locations.
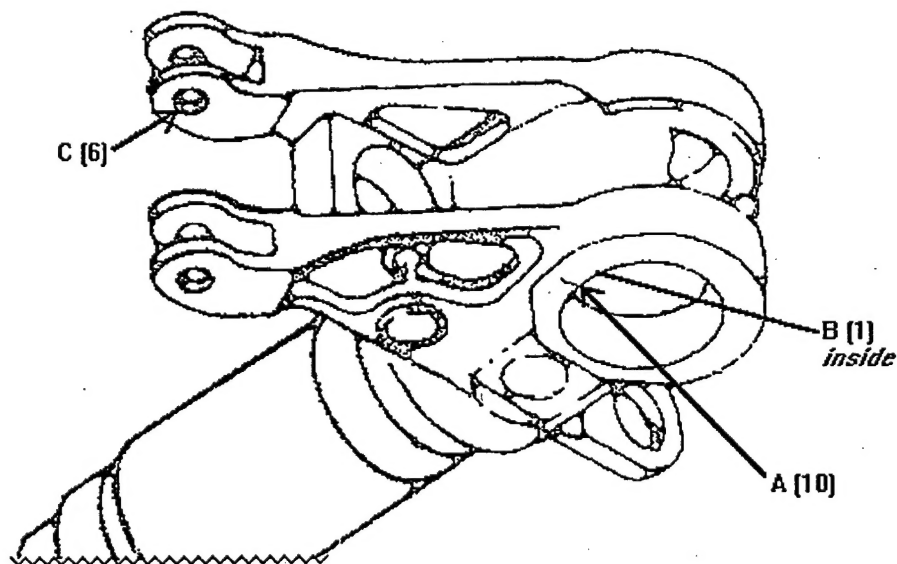Numbers in parentheses indicate number of cracked components.

Figure 6 Pitch Varying Shaft (PVS) Geometry and Crack Locations
Arrows and letters (A & B) designate crack locations.
Numbers in parentheses indicate number of cracked components.
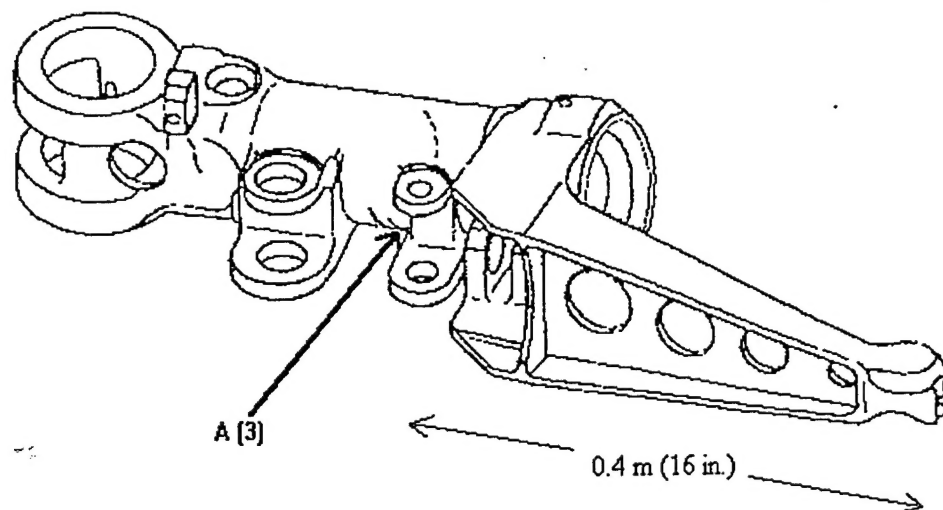
A [3]

0.4 m (16 in.)

Figure 7 Pitch Varying Housing (PVH) Geometry and Crack Locations
Arrow and letter (A) designates crack location.
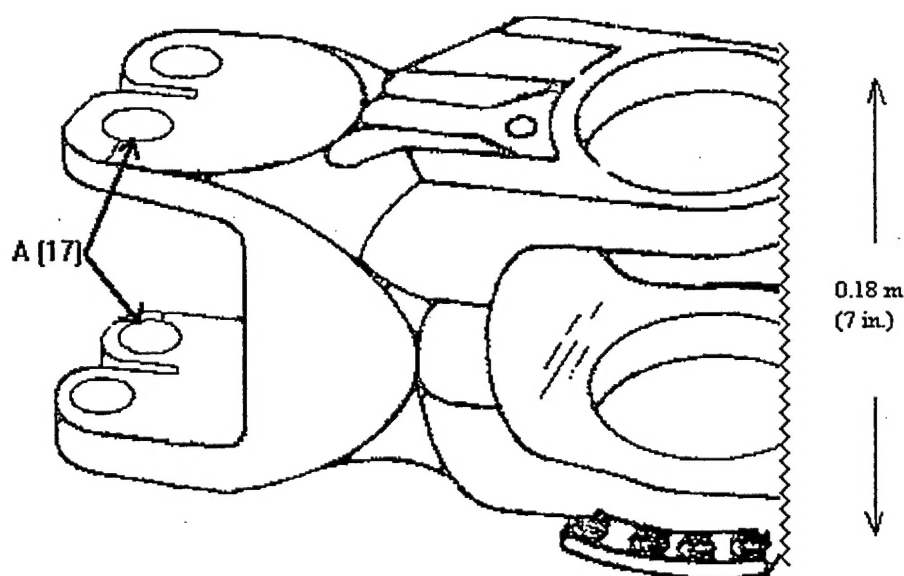Number in parentheses indicates number of cracked components.

A [17]

0.18 m
(7 in.)

Figure 8 Blade Attachment Fitting (BAF) Geometry and Crack Locations
Arrows and letter (A) designate crack locations.
Number in parentheses indicates number of cracked components.

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